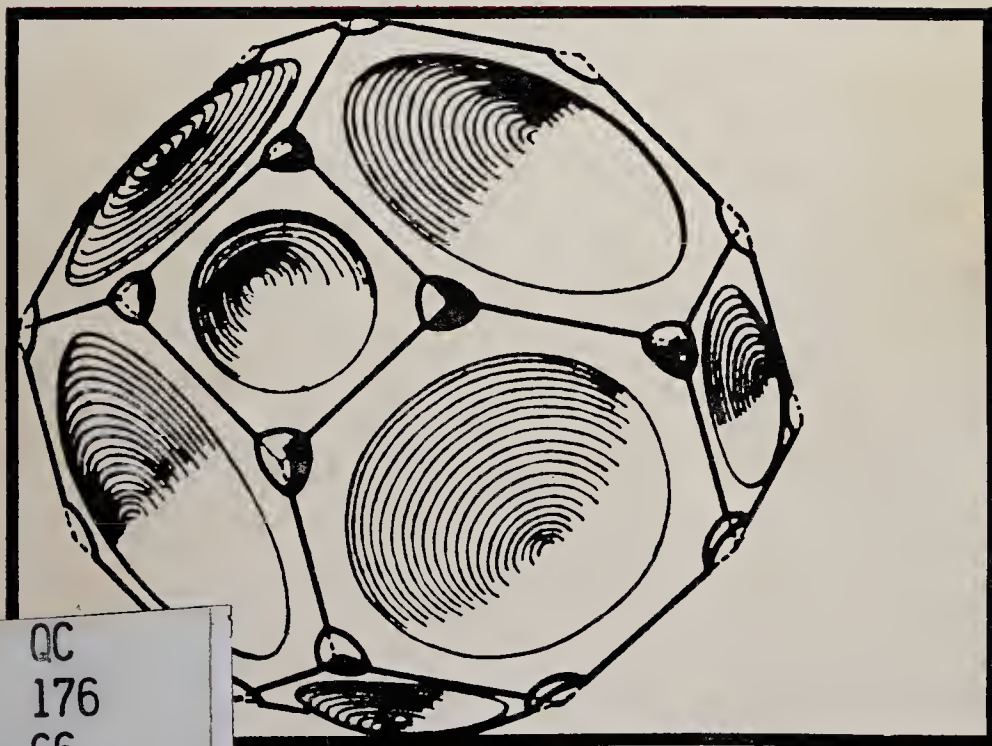


H. J. Goldsmid

THE THERMAL PROPERTIES OF SOLIDS



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SOLID-STATE PHYSICS

Edited by L. Jacob

SOLID-STATE PHYSICS

A new series edited by L. Jacob

This series of monographs has been designed to enable all undergraduates in the sciences—engineers, metallurgists, chemists, physicists, mathematicians, and biologists, to get some understanding of basic concepts and principles in a field fundamental to their own—the 'solid state' of matter. For this reason, the exposition has been made simple, and the approach, while based on classical lines, is supplemented and refined by the application of quantum mechanical ideas. 'Old' effects are explained, 'new' ones interpreted and future advances indicated.

It is hoped that the evidence here presented from experiment and supported by theory, will provide a reasonably unified picture of behaviour in the 'solid state'. Each main topic is so treated as to indicate facets of the enchanting interaction between atoms which go to form the pattern of a solid; an intelligent appreciation of this pattern of behaviour allows us to predict future possibilities in the materials with which we work.

The expansion of knowledge and broadening of our ideas following a reading of these texts should prove of the greatest value to all future scientists and teachers.

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The Thermal Properties of Solids

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Solid-State Physics

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Electron and Ion Emission from Solids

R. O. Jenkins and W. G. Trodden

The Thermal Properties of Solids

H. J. Goldsmid

Solid Semiconductors

A. K. Jonscher

Electrical Conduction in Solids

H. Inokuchi

Low Temperature Behaviour of Solids

R. G. Scurlock

The Thermal Properties of Solids

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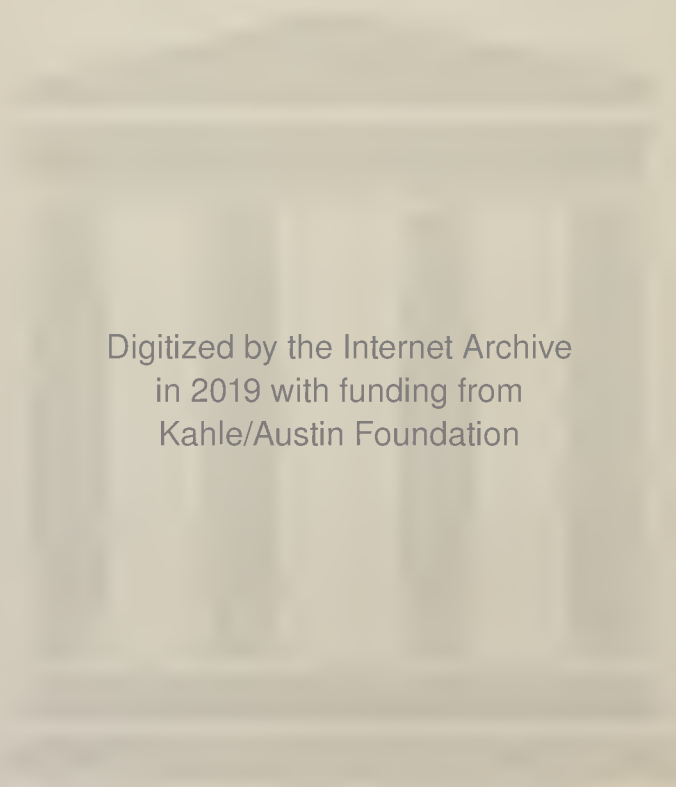
Preface

My aim in writing this short book has been to introduce the average student, with no more than an elementary knowledge of physics or mathematics, to the thermal properties of metals, insulators and semiconductors. The reader is most likely to encounter practical problems that are associated with the flow of heat and for this reason, particularly in the first chapter on experimental techniques, I have laid greater emphasis on thermal conductivity than on thermal capacity and expansion.

A brief outline of the background solid-state theory in Chapter 2 is followed in the next two chapters by the discussion of the thermal properties of the crystal lattice and of the electrons in metals. In the last chapter, the treatment of the thermoelectric effects in semiconductors leads on naturally to discussion of the very interesting bipolar heat conduction effect and of the bipolar thermomagnetic effects that are just beginning to find practical application. Finally, I mention the fascinating phenomenon of phonon-drag that will surely provide a fruitful field for future research.

I wish to thank Dr. L. Jacob and Dr. B. Yates for their most helpful advice during the planning of the book.

H. J. GOLDSMID



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1 Thermal Properties and Their Measurement

1.1. Specific Heat

The specific heat of any material is defined as the quantity of heat that raises the temperature of unit mass by one degree. Experiments always yield the specific heat c_p at constant pressure whereas it is the specific heat c_v at constant volume that is of more direct interest to the theoreticians. The specific heats at constant pressure and constant volume are related to one another by the expression

$$c_p - c_v = \beta_v^2 T / \chi \rho \quad (1.1)$$

where β_v is the volume coefficient of expansion, T is the absolute temperature, χ is the compressibility and ρ is the density.

Many of the early experiments on the specific heat of solids were carried out using the method of mixtures. In this method a sample of material is heated to some temperature T_1 and then immersed in a liquid (usually water), of known specific heat, at a temperature T_0 . Thereupon the sample and the liquid reach a temperature T_2 . The ratio of the thermal capacity (i.e. the product of specific heat and mass) of the solid to that of the liquid is equal to $(T_2 - T_0)/(T_1 - T_2)$. It is, of course, necessary to make corrections for heat losses to the surroundings and it is desirable that these losses should be kept as small as possible.

In most of the modern methods for the determination of specific heats, the sample is heated electrically at a known rate and its rate of rise of temperature is measured. The classical

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instrument, which illustrates this technique, is the Nernst vacuum calorimeter. It was designed specifically for use at low temperatures where much of the theoretical interest lies.

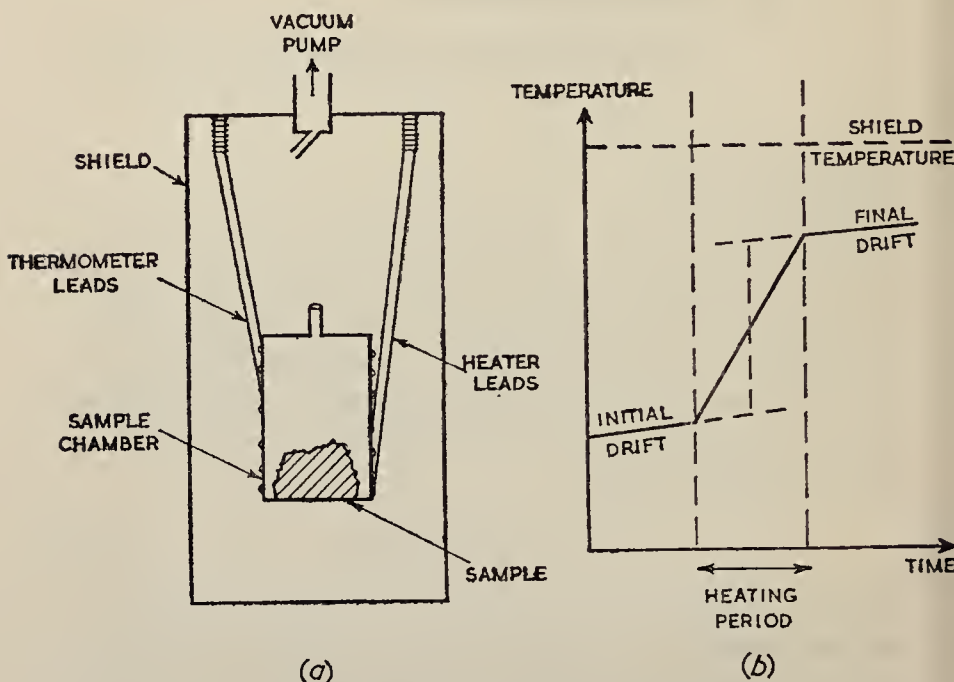


FIG. 1. The Nernst vacuum calorimeter.
(a) Schematic experimental arrangement.
(b) Simplified temperature-time plot.

The Nernst calorimeter is shown in one of its forms in Figure 1(a). The sample chamber is suspended inside a heat shield, which is maintained at a temperature close to that at which the specific heat is required. Thermal contact between the sample and its sealed container is ensured by the presence of a small quantity of exchange gas. After the temperature of the sample has reached a value close to that of the heat shield, the space inside the latter is evacuated. Heat transfer between the sample chamber and its surroundings is then due almost entirely to con-

duction along the fine leads to the heater and resistance thermometer, there being little heat radiation at low temperatures. The temperature of the sample chamber is recorded as a function of time, before, during and after a measured amount of energy is supplied to the heater. A schematic plot of temperature against time is shown in Figure 1(b). The rise of temperature of the sample, that would have resulted in the absence of heat transfer to the surroundings, is obtained by extrapolation of the plots of initial and final drift to the middle of the heating period.

If the material under test is an easily-machined metal, the heater and resistance thermometer wires can be wound on to a cylindrical specimen directly, and the sample chamber shown in Figure 1(a) is no longer necessary.

1.2. Expansion Coefficient

The linear expansion coefficient β of a body is defined as the increase of length per unit length when the temperature of the body is raised by one degree. The coefficient of cubical expansion or volume coefficient β_v is three times the linear coefficient for an isotropic solid.

The accurate measurement of the linear expansion coefficient requires a technique for the precise determination of very small changes of length. One of the commonest methods was devised by Fizeau and makes use of interference fringes between the plane polished face of the test specimen and a similarly prepared glass plate. The fringes, whose spacing depends on the angle between the two surfaces, move across the field of view as the specimen expands. The position of the glass plate is fixed by three screws which pass through the platform on which the specimen rests. The expansion coefficient of the screws can be determined by observing the motion of interference fringes produced between the glass plate and the platform with no specimen in place.

THERMAL PROPERTIES AND THEIR MEASUREMENT

In a more convenient version of the interferometric apparatus the sample is in the form of a hollow cylinder which rests on a plane polished platform. Interference fringes are observed between the platform and a flat glass plate that rests on top of the sample. In this case, the absolute expansion coefficient is determined directly.

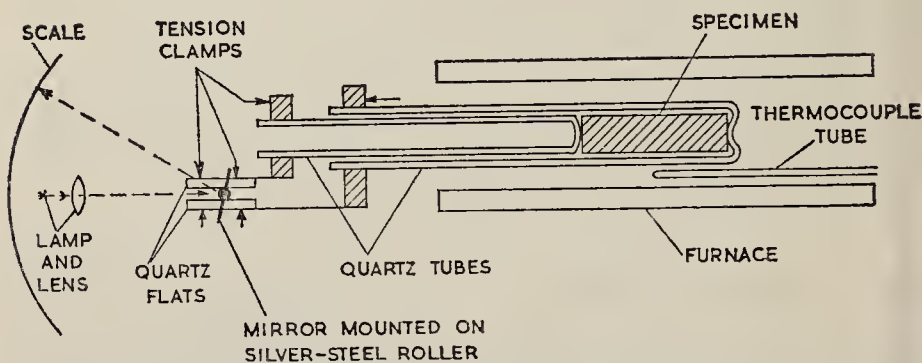


FIG. 2. Thermal expansion apparatus based on the principle of the optical lever.

Another popular technique employs the principle of the optical lever. An apparatus that makes use of this principle is shown in Figure 2; it is intended for operation up to about 1000°K . The expansion of the specimen relative to quartz causes one of the quartz tubes to slide within the other. The relative movement leads to rotation of the mirror which is detected using a lamp and scale. The displacement of the light spot on the scale is R/r times the relative change in length of the specimen, R being the distance between the mirror and the scale, and r the radius of the roller on which the mirror is mounted. It will be appreciated that the absolute expansion coefficient of the specimen cannot be determined by this method unless the expansion coefficient of the quartz is known.

The expansion coefficient of any material becomes very small at low temperatures but it is in this region that some of the most interesting behaviour is to be found. It is, therefore, particularly important that ultra-sensitive techniques should be available for low temperature studies. Perhaps the most sensitive method available at present is one in which the electrical capacitance between the test sample and a fixed plate is measured using a specially designed bridge circuit. Expansion or contraction of the sample alters this capacitance, the changes in which can be determined to a very high degree of precision. In fact, it is claimed that length changes as small as 10^{-8} cm can be detected and that measurements to 10^{-9} cm might be possible in the future.

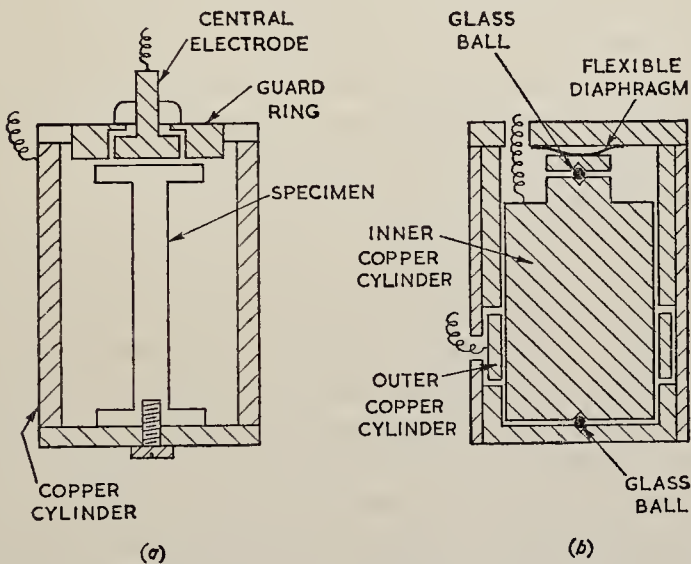


FIG. 3. Measurement of thermal expansion by G. K. White's capacitance method.

- (a) Differential expansion cell.
 (b) Absolute cell.

The expansion cells used in this method are shown schematically in Figure 3. In the differential cell (Figure 3(a)) the expansion of the specimen relative to the surrounding copper cylinder is observed. The expansion coefficient of copper is found using the 'absolute' cell shown in Figure 3(b), where the spacing between the inner and outer cylinders changes as the copper expands or contracts.

1.3. Thermal Conductivity

The thermal conductivity κ of a material is the rate at which heat is conducted across unit cross-sectional area when there is unit temperature gradient perpendicular to this area.

Most of the really accurate measurements of thermal conductivity at and below room temperature make use of the static, absolute method. Heat is supplied at a known rate to one end of the test sample and removed from the other end by a heat sink that is kept at a fixed temperature. The thermal conductivity is found in terms of the measured temperature gradient associated with the flow of heat.

The dimensions of the sample and the method of determining the temperature gradient depend on the order of magnitude of the thermal conductivity. When the thermal conductivity is low (as it is in many electrical insulators) it is important that the lateral heat losses should be kept as small as possible. Thus, the ratio of length to cross-section area is made low and this also assists the experimenter by reducing the time taken to reach thermal equilibrium. Of course, it is difficult to measure the temperature gradient accurately when the length is small, since the thermometers cannot then be attached to the sample itself. In practice, for poor conductors of heat, the thermometers are attached to the source of heat and the sink, great care being taken to reduce the thermal resistance at the contacts with the sample to the lowest possible value. The surfaces of contact are

made smooth and flat and, if the sample cannot be soldered in place, some liquid such as glycerine is applied at the interfaces. The actual value of the contact resistance can be determined if samples of different length are employed in successive experiments.

If it is at all convenient, a guard-ring should surround the sample; otherwise corrections must be made for heat radiation from the exposed surfaces. In any case, the surrounding space should be evacuated to pressures below about 10^{-5} mm Hg to eliminate air-conduction and convection losses. The required degree of vacuum can best be determined using a Pirani gauge, since this instrument is based on the pressure dependence of the thermal conductivity in a low-pressure gas.

When the thermal conductivity is reasonably high, as it is for most metals, the lateral heat losses become rather less important than the contact resistances. It is then vital that the thermometers should be attached to the sample itself. Thus, a precise determination of the temperature gradient can be made only if the length of the sample is large compared with its width.

Most solids become much better conductors of heat at low temperatures than at room temperature while radiation losses rapidly become less important as the temperature is reduced. Thus most of the low-temperature measurements make use of long rather than short samples. One piece of apparatus is illustrated schematically in Figure 4 and has been used for semiconductors and metals at and above liquid helium temperatures. Typical sample dimensions for this apparatus are length 5 cm, and diameter one or two mm. A piece of resistance wire is wound around, and cemented to, one end of the sample; the other end of the sample is attached, via a copper bar, to the high pressure chamber of a Simon expansion liquifier. When measurements are required below 4.2°K (the boiling point of helium at atmospheric pressure) the chamber is filled with liquid helium which is allowed to boil under reduced pressure. Above

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10°K liquid hydrogen is used as the coolant while above 55°K liquid oxygen is employed. Temperature control at some of the intermediate temperatures is achieved by means of the heating element wound on the copper bar.

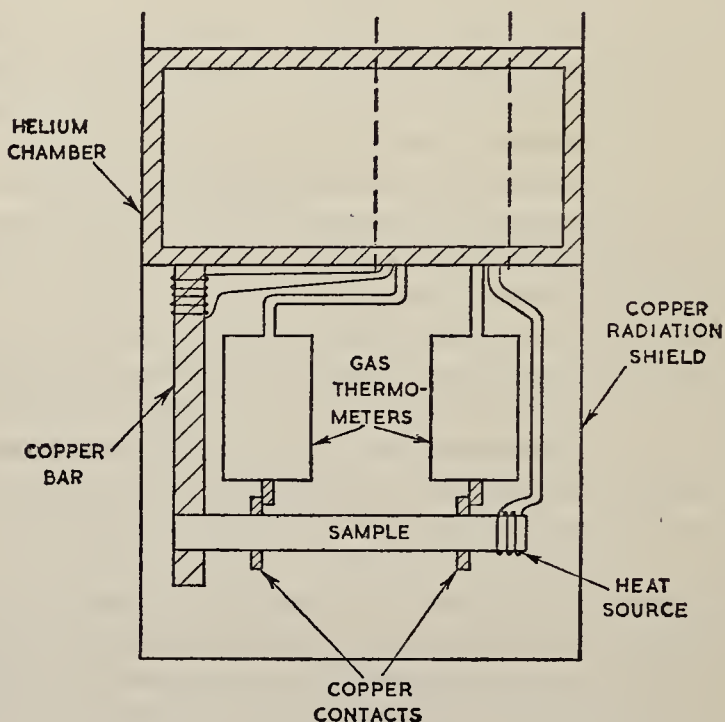


FIG. 4. H. M. Rosenberg's low-temperature thermal conductivity apparatus.

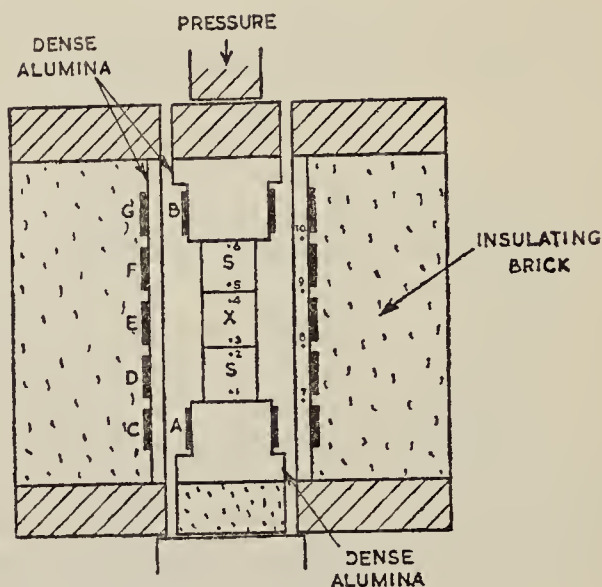
Helium-gas thermometers are used for measuring the temperature gradient in the above apparatus but carbon- or germanium-resistance thermometers could also be employed. Thermocouples are convenient and are usually adopted for measurements of temperature at and above that of liquid nitrogen (77°K) but, until recently, sensitive and reproducible thermocouples for the liquid helium and liquid hydrogen temperature

ranges were not available. Now, however, the use of a dilute alloy of iron in gold as a thermoelectric material seems to have made possible accurate measurements with thermocouples at low temperatures.

It is often difficult to make a precise absolute determination of the thermal conductivity of a solid at some elevated temperature. This is because of the increased radiation losses from the exposed surfaces of the heater as the temperature is raised. When the dimensions of the sample are large the losses are proportionately less than when they are small, and the guard-ring principle can be applied quite easily. However, when only small specimens of the material are available, it is better to use a comparison method. Here the same quantity of heat is made to pass through the test sample and a standard sample, the thermal conductivity of which is known; the temperature gradients in the two materials are then compared with one another.

An apparatus that has been used for ceramics up to 1000°C is shown in Figure 5. The samples are one-inch cubes, pressed together between two dense alumina blocks. Two standard samples (one on either side of the test sample) are employed so as to minimise errors due to lateral heat flow. In order to avoid errors due to thermal resistance at the contacts, the measuring thermocouples are wedged into fine holes that are drilled in all the samples. If there were any excessive resistance at the contacts, it would be difficult to provide effective shielding against heat losses, so sheets of silver foil (or platinum foil if above 900°C) are interposed between the surfaces.

The temperature gradient in the column is established first using the heaters A and B and then the auxiliary heaters C-G are utilised in preventing the lateral flow of heat. When the power supplies to these auxiliary heaters are correctly adjusted, the distribution of temperature in the column is matched by that in the surrounding alumina shield.



- 1-10 Pt-Pt-10% Rh THERMOCOUPLES
 A-G HEATING ELEMENTS
 S STANDARD SAMPLES
 X TEST SAMPLE

FIG. 5. J. Francl and W. D. Kingery's apparatus for comparison of thermal conductivities.

Although dense alumina was originally used as the standard material, there are a number of other substances on which accurate absolute measurements of the thermal conductivity have been made. Generally speaking it is best to use, as standards, samples that have a thermal conductivity which is of the same order as the estimated value for the test sample.

Although the static methods described above usually lead to more accurate values for the thermal conductivity than can be obtained using dynamic methods, they require a considerable time for the completion of a set of observations. Not all the dynamic methods are inaccurate, however, and it has been claimed that the errors are no more than about 4% for the

apparatus illustrated in Figure 6. The test sample is clamped between two copper blocks by means of the vertical screw. The bridge which carries this screw is insulated from the lower copper block by the methyl methacrylate walls of the apparatus.

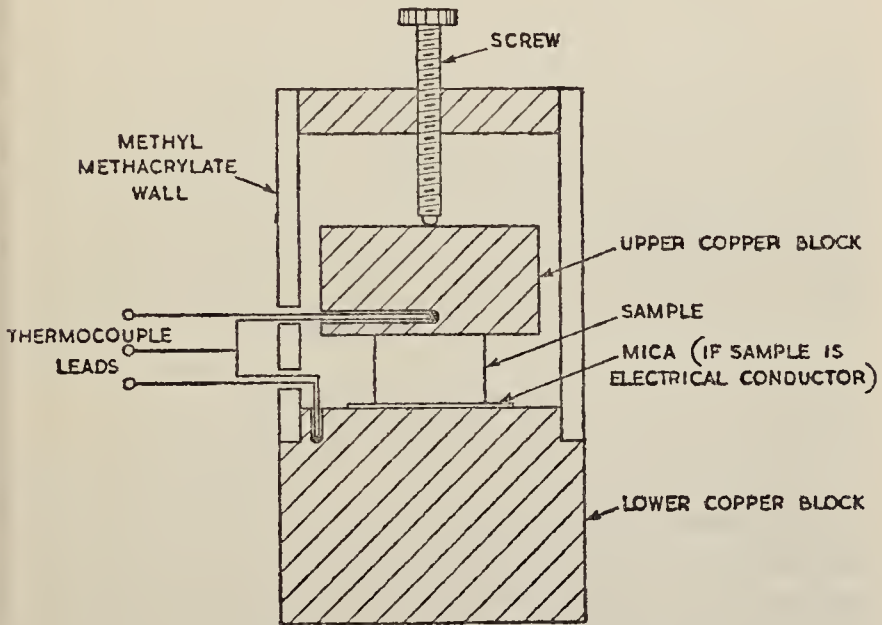


FIG. 6. A. V. Ioffe and A. F. Ioffe's dynamic method for the measurement of thermal conductivity.

Copper-constantan thermocouples are inserted in the copper blocks in the neighbourhood of the sample. If the sample is an electrical conductor, a thin sheet of mica is interposed between it and the lower block to ensure electrical insulation; thus, the temperature difference can be measured using the thermocouples connected differentially as shown.

The whole apparatus is at first brought to a uniform temperature. Then the lower block is immersed in a cooling bath, and the temperature difference between the blocks and the absolute temperature of one of them are continuously recorded. If, at

some time t the temperatures of the upper and lower blocks are T_2 and T_1 respectively,

$$\kappa(T_2 - T_1)A/l = C_2 dT/dt \quad (1.2)$$

where κ is the thermal conductivity of the sample, A is its cross-section area and l is its length. C_2 is the thermal capacity of the copper block that is assumed to be very much greater than that of the sample. In a practical experiment the thermal capacity of the sample cannot usually be neglected, but the correction to be applied because of this is usually quite small. The need for another correction arises through the heat transfer between the upper block and the surrounding walls; it can be calculated from the measured temperature difference between the upper and lower blocks when equilibrium has been reached. A further correction, for heat transfer between the two blocks through the air surrounding the specimen, can be determined by conducting an experiment with a sample that is a very poor conductor of heat, e.g. a block of paper. Convective heat transfer is negligible since the lower of the two blocks is the cooler. Finally, some allowance must be made for the thermal resistance of the mica insulation (if present) and for any other resistance between the sample and the blocks; the resistances at the contacts are said to be negligible if the surfaces are ground flat, and if gallium, an amalgam, glycerine or oil is interposed.

1.4. Thermal Diffusivity

A quantity that is closely related to the thermal conductivity is the thermal diffusivity k_d which is defined as $\kappa/c\rho$, where c is the specific heat and ρ is the density. It is a measure of the rate at which a disturbance in the temperature of one part of a body travels to any other part; it is also a measure of how little the disturbance is attenuated as it travels from point to point.

The thermal diffusivity of a material can be measured by Ångström's method, in which a sinusoidal temperature variation is applied to one end of a very long bar, and the variation of temperature with time is observed at two points on the bar. If there is no exchange of heat between the surfaces of the sample and its surrounding enclosure, it can be shown that

$$k_d = \omega l^2 / 2 \ln^2 \alpha = \omega l^2 / 2 \beta^2 \quad (1.3)$$

where ω is the angular frequency of the applied temperature variation. α is the ratio of the amplitudes of the temperature wave at the two points separated by a distance l , and β is the corresponding phase difference $\ln \alpha$ being equal to β . When the surface heat losses are appreciable, $\ln \alpha$ and β become unequal but the thermal diffusivity is still given by a simple expression, namely,

$$k_d = \omega l^2 / 2 \beta \ln \alpha \quad (1.4)$$

It is possible to calculate the surface losses from the difference between $\ln \alpha$ and β .

The fact that the thermal diffusivity can be obtained so simply has led to the fairly widespread use of this and similar methods in the indirect determination of the thermal conductivities of solids at high temperatures. One attractive feature is the elimination of the corrections for heat losses that are very important in conventional thermal conductivity measurements at high temperatures. Another advantage arises from the fact it does not matter if the contact between the heat source and the sample is poor. A disadvantage of this type of measurement is that the specific heat and the density must also be determined before the thermal conductivity can be calculated.

The recent measurement of the thermal diffusivity of germanium and other electrical conductors at elevated temperatures, using a variable transformer controlled by a specially-shaped cam to generate a sinusoidal temperature wave, provides evidence for the accuracy of Ångström's method. In fact,

it does not matter if the wave form is not quite perfect since the higher harmonics are very rapidly attenuated (see Equation (1.3)). The variations of temperature at the two points on an electrically conducting sample can be detected from the thermoelectric voltages picked up by wires attached at these points; in effect, the sample then acts as its own thermoelectric thermometer, so that there is no question of imperfect contact between thermometer and sample.

It is recognised that thermal diffusivity measurements can be very useful at low temperatures. When the temperature is close to the absolute zero, the specific heat of a solid is very small and, therefore, difficult to measure. On the other hand, the thermal conductivity should be no more difficult to determine than at higher temperatures. Thus, if the thermal diffusivity and the thermal conductivity are measured, the specific heat can be calculated.

1.5. Thermoelectric and Thermomagnetic Coefficients

The thermal properties of a solid are often of importance in determining its suitability for any particular application. For example, if it is necessary that the substance should be capable of withstanding severe thermal shock without fracture, its thermal expansion coefficient should be low and its thermal conductivity should be high (its mechanical properties should, of course, also be good). The thermal conductivity is a property of great significance in the consideration of materials for thermoelectric generation or refrigeration. A good thermoelectric material should have a high ratio of electrical conductivity to thermal conductivity since this minimises the irreversible effects due to Joule heating and heat conduction; the Peltier or Seebeck coefficient should, of course, be large too.

The absolute Seebeck coefficient α of a material is defined as the potential gradient that arises when it is subjected to unit temperature gradient. The absolute Peltier coefficient π is the

quantity of heat that is transported by unit quantity of electricity flowing in the material. It should be noted that the Seebeck and Peltier effects are revealed only when one forms a junction between one material and another; thus, any practical experiment determines the difference between the Seebeck or Peltier coefficients of the two materials.

There is a third thermoelectric coefficient, the Thomson coefficient τ , which is defined as the rate of reversible heat generation or absorption in a length of material that is subjected to unit temperature difference, when unit electric current is passed.

The Seebeck, Peltier and Thomson coefficients are related to one another by the thermodynamic equations

$$\pi = \alpha T \quad (1.5)$$

and

$$\tau = T \, d\alpha/dT \quad (1.6)$$

Equations (1.5) and (1.6) are known as Kelvin's laws.

The absolute Seebeck coefficient of a given conductor can be determined as follows. At very low temperatures, the differential Seebeck coefficient is measured for a junction between the conductor and a superconducting metal or alloy; since the differential Seebeck coefficient between any pair of superconductors is zero, it is reasonable to assign zero absolute Seebeck coefficient to any superconductor. The Thomson coefficient is then measured from these very low temperatures up to high temperatures. The high-temperature absolute Seebeck coefficient can be evaluated using Equation (1.6) in integral form,

$$\alpha_2 - \alpha_1 = \int_{T_1}^{T_2} (\tau/T) \, dT \quad (1.7)$$

where α_2 and α_1 are the absolute Seebeck coefficients at the high and low temperatures T_2 and T_1 respectively. This method has been applied to the metal lead using the superconducting compound Nb_3Sn (which has a transition to the normal state at about 18°K), for the low temperature measurements.

The Seebeck coefficient and the thermal conductivity of an electrical conductor are, in general, altered when a magnetic field is applied (usually in the transverse direction). The change in Seebeck coefficient is known as the magneto-Seebeck effect or longitudinal Nernst effect, while the change in thermal conductivity is called the magneto-thermal resistance effect or Maggi-Righi-Leduc effect.

When there is a flow of heat through a body in a transverse magnetic field, there appears, in the mutually perpendicular direction, a potential gradient (the Nernst effect) and a temperature gradient (the Righi-Leduc effect). Similarly, when an electric current flows through a material, the action of a magnetic field leads to a transverse potential gradient (the Hall effect) and temperature gradient (the Ettingshausen effect). The four transverse thermomagnetic coefficients are defined in Table 1.

TABLE 1. Definition of the Transverse Thermomagnetic Coefficients

Name of coefficient	Experimental conditions	Observed quantity	Definition of coefficient
Hall	$i_x \neq 0, i_y = \nabla_x T = \nabla_y T = 0$	E_y	$R = E_y/Hi_x$
Ettingshausen	$i_x \neq 0, i_y = \nabla_x T = w_y = 0$	$\nabla_y T$	$P = \nabla_y T/Hi_x$
Nernst	$\nabla_x T \neq 0, i_x = i_y = \nabla_y T = 0$	E_y	$Q = E_y/H\nabla_x T$
Righi-Leduc	$\nabla_x T \neq 0, i_x = i_y = w_y = 0$	$\nabla_y T$	$S = \nabla_y T/H\nabla_x T$

Primary flow in x -direction, magnetic field H in z -direction

i = electric current density, w = heat flux density, E = electric field, ∇T = temperature gradient.

Usually the thermomagnetic effects are rather small, but under some conditions (as will be discussed in Chapter 5) they can become large and, at low temperatures, the Nernst and

Etingshausen effects can be at least as effective as the Seebeck and Peltier effects in energy conversion devices. It should be noted that the Nernst and Etingshausen coefficients are thermodynamically related to one another by the equation

$$\kappa P = QT \quad (1.8)$$

This equation may be compared with the Kelvin relation Equation (1.5).

It will be appreciated that the experimental condition (the so-called 'isothermal' condition) for the measurement of the Nernst coefficient that has been given in Table 1 is very difficult to apply in practice. Usually one measures the 'adiabatic' Nernst coefficient Q_a for which the condition $\nabla_y T = 0$ is replaced by the condition $w_y = 0$. The isothermal Nernst coefficient Q , which is far more meaningful from the theoretical viewpoint, can be calculated from the adiabatic Nernst coefficient only if the Righi-Leduc and Seebeck coefficients are also known since

$$Q = Q_a + \alpha S \quad (1.9)$$

Because of this inter-dependence of the various coefficients, it is desirable that as many of them as possible should be determined in the same experiment.

Figure 7 shows an experimental arrangement that has been used in work on semi-metals at liquid nitrogen temperature. Leads 1 and 3 are used for measuring the longitudinal electric field and leads 2 and 3 for determining the transverse electric field. Similarly the longitudinal temperature gradient is found from the thermocouples 1-4 and 3-6, while the transverse temperature gradient is found using the couples 2-5 and 3-6. When the primary flow is an electric current, it passes through the specimen via the copper heat sink and heat source. The heavy copper lead to the heat source (not shown in the diagram) is disconnected during thermal conductivity measurements,

THERMAL PROPERTIES AND THEIR MEASUREMENT

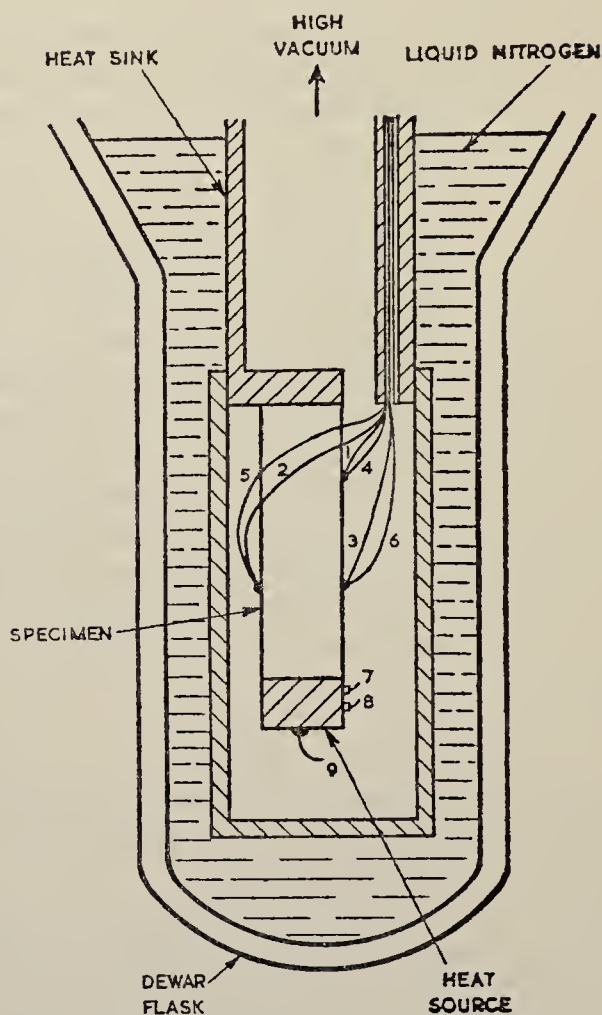


FIG. 7. Apparatus for measurement of the thermogalvanomagnetic coefficients.

1, 2, 3 Chromel wires. 4, 5, 6 Alumel wires.

7, 8 Connections for heater leads.

9 Connection for current lead to specimen
(heater leads and current lead not shown).

since it would provide a substantial thermal shunt to the sample; the high vacuum ensures near-adiabatic conditions.

2 Insulators, Metals and Semi-conductors

2.1. Interatomic Bonds and the Crystal Lattice

A solid body is generally made up of one or more crystals, in each of which the atoms are arranged on a more or less regular lattice. An amorphous solid is an exception though it does retain some short-range order, i.e. any group of closely neighbouring atoms is not arranged in a completely random way.

The particular crystal structure favoured by an element or compound depends largely on the way in which the atoms are bound to each other. One of the simplest types of bond arises from the Coulomb attraction between ionized atoms with charges of opposite sign. The charging of the atoms in turn arises from the tendency for the formation of closed electric shells. Thus, an alkali metal such as sodium has only one electron outside its closed shells, and it is easy for this electron to be detached; the alkali metals are said to be strongly electro-positive. Likewise, the halogens are strongly electronegative since there is a tendency for a neutral halogen atom to take up the one electron that is needed to complete its outer shell. Ionic binding is thus favoured in compounds between highly electro-positive and electronegative elements. The alkali halides (e.g. sodium chloride) form cubic crystals in which each positive or negative ion is surrounded by six nearest neighbours with charges of the opposite sign. It will be realised, of course, that the Coulomb attraction between ions of opposite sign must change to a predominantly repulsive force as the distance

between the ions decreases below that for the equilibrium position in the natural crystal.

The binding in a non-metallic element such as diamond, or in a compound between two elements of similar electronegativity, results from the sharing between neighbouring atoms of the electrons in the incomplete outer shells. A carbon atom in diamond has four outer electrons, each of which is shared with another atom; thus, in a diamond-type crystal each atom has four nearest neighbours. The very strong bonds that arise from the sharing of electrons are called covalent. In a covalent crystal the binding electrons are found close to the lines that join neighbouring atoms, i.e. the bonds are directed, whereas in ionic crystals the outer electrons tend to form spherical clouds around the electronegative atoms.

Metallic binding is likewise due to the sharing of electrons, but in metals all the outer electrons are shared between all the atoms. Here it is unnecessary that the number of nearest neighbours should be related to the valency of the elements, and it is found that many metals take up one of the two crystal structures in which there is very close packing; these are the face-centred cubic and close-packed hexagonal structures.

Atoms which are electrically neutral are held together by the rather weak van der Waals-type of bond resulting from the small periodic dipole moments possessed by the neutral atoms; it is responsible for the binding in the condensed inert gases.

The assumption that the atoms of a crystal are arranged in a perfectly regular fashion is, at best, no more than a good approximation. For example, in a real crystal there are various types of point defect associated with vacancies, substitutional and interstitial impurities; there are also the 'line' defects known as 'dislocations'. Even if all these defects were absent, the strict periodicity of the lattice would still be disturbed, at any temperature above the absolute zero, by the thermal vibrations of the atoms.

The atomic vibrations have a predominating influence on the thermal properties of solids. Thus, when a solid is heated, most of the energy that is supplied is used in increasing the amplitude of the vibrations. Because the interatomic forces do not strictly obey Hooke's law, the increased amplitude of vibration as the temperature is raised leads, in general, to thermal expansion. Heat conduction in electrical insulators is due to the transfer of vibrational energy from atom to atom.

The atoms do not, of course, vibrate independently of one another, since they are linked together by the interatomic bonds. It is convenient, then, to consider, not the vibrations of the individual atoms, but rather the vibrational waves that extend throughout the whole crystal. The periodic nature of the crystal lattice implies that only certain modes of vibration (the so-called normal modes) are permissible; these are characterised by specific values of wavelength and frequency. Furthermore, the amount of energy in each mode can only amount to an integral (or zero) number of quanta; these quanta are usually known as 'phonons'.

In discussing the thermal conductivity of the lattice it is customary to think, not of the collective vibrations extending through the whole crystal, but of the 'phonon' wave packets arising from the interference between normal modes of slightly different frequency. The use of the term 'phonon' in this book usually implies that one of these wave packets is being considered.

2.2. The Free Electron Theory of Metals

The free electron theory of metals was first presented by Drude and later developed by Lorentz and others. It was based on the assumption that all except the outer electrons of the atoms in the metal are tightly bound. The outer electrons were supposed to form an electron gas having properties that could be deter-

mined from the kinetic theory of gases. In particular, it was assumed that thermal energy would be distributed among the electrons according to the classical Maxwell-Boltzmann statistics, the mean energy being $3kT/2$, where k is Boltzmann's constant.

The classical free electron theory had some success in explaining the properties of metals. It gave a reasonable value for the electrical conductivity, assuming the number of free electrons to be equal to the number of atoms, and the electron free path to be of the order of the interatomic spacing. The theory indicated that the electrical conductivity should fall with increasing temperature as is found in practice (though it gave the wrong power-law for the temperature-dependence). A triumph of the classical theory was its explanation of the Wiedemann-Franz law which states that the ratio of the thermal conductivity to the electrical conductivity is the same for all metals at a given temperature.

Certain features of the classical theory, however, make it untenable. One of the most convincing proofs that it is invalid is provided by the fact that the specific heat of a metal at ordinary temperatures has the value $3k$ per atom, the same value as for an electrical insulator. If the electrons really behaved as a classical gas they should make an appreciable contribution to the specific heat.

Sommerfeld showed that some of the shortcomings of the classical theory can be overcome if account is taken of the fact that a free electron gas obeys Fermi-Dirac statistics rather than Maxwell-Boltzmann statistics. In other words the classical theory must be replaced by the quantum theory. According to the laws of quantum statistics

- (i) electrons can have spins with quantum numbers $\frac{1}{2}$ or $-\frac{1}{2}$ but otherwise they are indistinguishable from one another,

- (ii) electrons reside in discrete energy states with characteristic values for the momentum,
 and (iii) there can be no more than one electron with a given spin in a given energy state (the Pauli exclusion principle).

Sommerfeld showed that, in unit volume of free space, the number of allowed electronic states with energies lying between ε and $\varepsilon + d\varepsilon$ is

$$g(\varepsilon) d\varepsilon = \{4\pi(2m)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}/h^3\} d\varepsilon \quad (2.1)$$

where m is the mass of a free electron and h is Planck's constant.

The classical theory indicates that the energy of all electrons should be zero at 0°K . On the other hand, the quantum theory shows that, at this temperature, the n electrons merely occupy the states of lowest energy. At higher temperatures the distribution of electrons within the energy states is determined by the Fermi-Dirac distribution function

$$f(\varepsilon) = 1 / \left\{ \exp \left(\frac{\varepsilon - \zeta}{kT} \right) + 1 \right\}, \quad (2.2)$$

where $f(\varepsilon)$ is the probability that a state of energy ε contains an electron. ζ is called the Fermi energy and has such a value that

$$\int_0^\infty f(\varepsilon) g(\varepsilon) d\varepsilon = n, \quad (2.3)$$

where $g(\varepsilon)$ is the density of states at energy ε given by Equation (2.1).

Figure 8 shows the energy-distribution of the electrons at 0°K and at a temperature T that is much less than ζ/k (the so-called Fermi temperature). It should be noted that ζ/k is of the order of 10^4 or 10^5°K for typical metals, though it can be very much smaller for semiconductors and semi-metals. It will be seen that the electron distribution changes but little as the temperature is raised and it is immediately obvious why the electrons make only a small contribution to the specific heat.

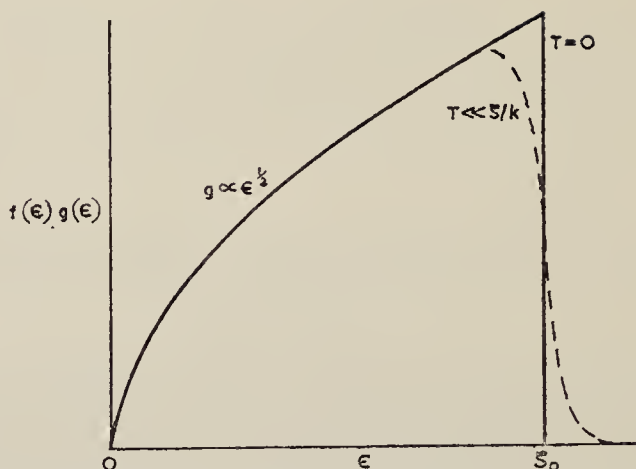


FIG. 8. Distribution of electrons with energy according to the free electron quantum theory. ζ_0 is the Fermi energy at 0°K .

If the temperature is much greater than ζ/k , which implies that the electron concentration must be very much less than that of the atoms in the solid, Equation (2.2) becomes

$$f(\epsilon) = \exp\left(-\frac{\epsilon - \zeta}{kT}\right), \quad (kT \gg \zeta). \quad (2.4)$$

This is the Maxwell-Boltzmann distribution function and, if the electron concentration is small enough for Equation (2.4) to be obeyed, the electron gas is said to be classical. On the other hand, if the temperature is much less than ζ/k the electron gas is termed 'degenerate'.

One consequence of 'degeneracy' is that only a small proportion of the outer electrons in a metal contribute to the conduction processes. The transport of charge through a solid requires the movement of electrons between energy states; as it moves from state to state an electron can change its energy in steps of no more than about kT . Vacant states are, thus, only accessible to electrons which have an energy within about kT of the Fermi energy.

Since so few electrons carry any current it is clear that their free path length must be much greater than that predicted by the classical theory. The free electron quantum theory does not explain why the free path length of the electrons should be large or why it should vary with temperature. It cannot explain the difference between metals and insulators, and it cannot account for the fact that certain electrical conductors have positive Hall coefficients. In order to explain these facts we introduce the band theory of solids.

2.3. Energy Bands

Since the electrons in a solid move, not in free space but in an array of atoms that are coupled together, it is hardly surprising that the free electron theory fails to account for all their properties. If it is assumed that the motion of each electron can be considered independently of that of the other electrons (this is the so-called one-electron model), the effect of all the remaining electrons and of the atomic nuclei is to provide a periodic potential that modifies the motion of the electron. Bloch showed that the wave equation of an electron moving in a periodic potential, whatever its precise form, has only certain solutions. It is characteristic of these solutions that they fall within certain bands of energy that are separated from one another by forbidden energy gaps.

In the simplest case the energy ε of an electron is zero when the wavevector \mathbf{k} is also equal to zero. Then, for a cubic crystal, the surfaces of constant energy in wavevector-space are spheres and ε is proportional to k^2 (in this case the wavevector may be replaced by the scalar wavenumber k)*. This situation is identical with that which exists for an electron in 'free' space; however, the constant of proportionality may be appreciably

*The wavenumber k is defined as $2\pi/\lambda$ where λ is the wavelength.

different because of the interaction between the electrons and the periodic potential. In both cases

$$\varepsilon = h^2 k^2 / 8\pi^2 m^* \quad (2.5)$$

where, for a free electron gas m^* is equal to the electronic mass m , but otherwise m^* must be regarded as an 'effective' mass. By using the 'effective' mass, instead of the 'free' electron mass the results of the free electron quantum theory can be adapted for electrons in energy bands. For example, Equation (2.1) gives the distribution of energy states within an energy band if m is replaced by m^* . In general, the effective mass is defined by the relation

$$1/m^* = (4\pi^2/h^2) \partial^2 \varepsilon / \partial k^2. \quad (2.6)$$

While Equation (2.5) may be true when ε is small, it cannot be true for large energies. It may be shown that near the top of an energy band the effective mass as defined by Equation (2.6) must become negative. In this situation, the crystal behaves as if it contained negatively-charged carriers of negative mass, but, in practice, it is usual to view the behaviour as that of positive carriers with positive mass. The positive carriers are known as 'holes' since they may be regarded as the empty states in a nearly-full energy band. This feature of energy band theory accounts for the positive Hall coefficients that are often observed.

If an energy band is either completely full or completely empty, the application of an electric field does not result in a flow of current. This is because there are either no electrons to carry the charge or no empty states into which electrons can move. Thus, the band theory differentiates between electrical insulators, in which all the continuous bands of energy are either full or empty, and electrical conductors in which at least one of the bands is only partly full.

At any temperature above 0°K , no solid is a perfect electrical insulator, since there must be some thermal excitation of electrons from the highest filled band to the nearest empty band across the forbidden energy gap. When the conductivity, due to thermal excitation across the energy gap, is appreciable, the solid is said to be an intrinsic semiconductor. In an intrinsic semiconductor the concentrations of conduction electrons and positive holes are equal, since each electron excited into the upper band leaves a hole in the lower band.

A solid, that is a poor electrical conductor in the pure state, can sometimes be made to conduct electricity quite readily by the introduction of impurities. If the impurities tend to donate electrons to the upper or conduction band they are said to be 'donors'. Materials that contain donor impurities conduct electricity by means of quasi-free electrons in the conduction band and are known as '*n*-type' extrinsic semiconductors.

Impurities that take up electrons from the valence band are known as 'acceptors' and give rise to localised energy levels, near the upper edge of that band, in the forbidden gap. The electrons excited into the acceptor levels leave behind positive holes in the valence band. The materials in which the conduction is due to these positive holes are known as '*p*-type' semiconductors.

Energy diagrams for the various types of non-metallic solid are shown in Figure 9. It will be seen that intrinsic semiconductors differ from insulators only in the width of the energy gap.

The number of charge carriers in a semiconductor is generally temperature-dependent because they are thermally excited either from the impurity levels or across the energy gap. In a metal, on the other hand, the concentration of conduction electrons is independent of temperature. This is either because the valence and conduction bands overlap one another or because one of the upper bands is only partly filled even at 0°K .

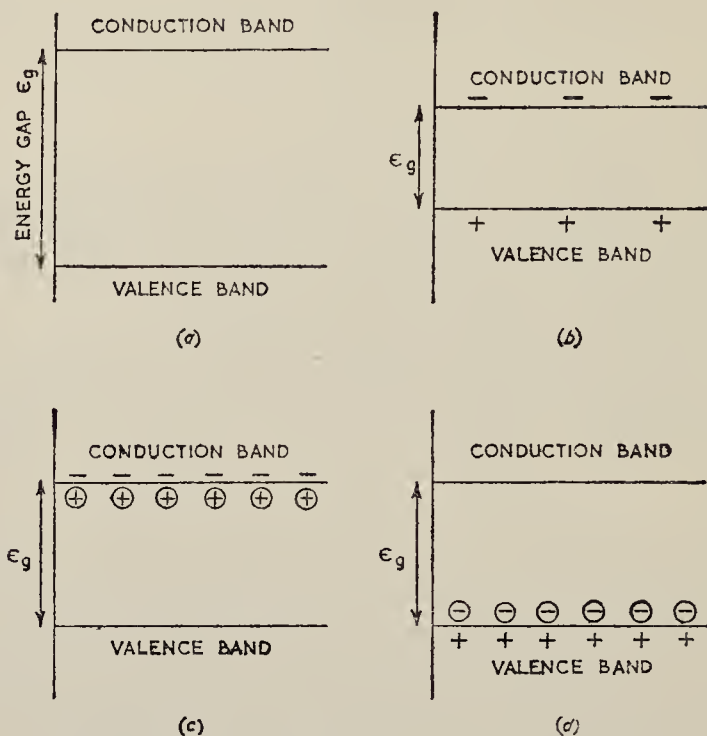


FIG. 9. Energy band diagrams for non-metallic solids.

(a) Electrical insulator. (b) Intrinsic semiconductor. (c) *n*-type extrinsic semiconductor. (d) *p*-type extrinsic semiconductor. —, +, mobile electrons and holes. \ominus , \oplus , electrons and holes in impurity states.

A semiconductor, then, differs from a metal in having a positive energy gap between a more-or-less full band and a more-or-less empty band. Semi-metals are materials in which there is overlap between the valence and conduction bands; however, the degree of overlap is so slight that semi-metals retain many of the characteristics of semiconductors.

If the crystal lattice were perfectly periodic the electrical conductivity would be infinite. However, the departures from perfect periodicity, due to either thermal vibrations or the various

types of defect, lead to scattering of the charge carriers. Scattering by the thermal vibrations is usually predominant at high temperatures and results in a mean free path that decreases with increasing temperature. This explains the fact that the electrical conductivity of a metal falls as the temperature is raised.

3 Properties of the Crystal Lattice

3.1. Vibrational Spectra and the Specific Heat

The well-known Dulong and Petit law states that the specific heat of any elemental solid is given by the expression

$$c_v = 3Nk/A \quad (3.1)$$

where A is the atomic weight and N is Avogadro's number. This law is explained by the classical theory using the equipartition principle—the total energy kT being associated with each of the three degrees of freedom of an atom in a solid. Thus, the internal energy U per gram atom is equal to $3NkT$ and the specific heat C_v per gram atom, given by $(\partial U/\partial T)_v$, is $3Nk$. Actually, Equation (3.1) is also applicable to compounds if A is regarded as the mean atomic weight.

Dulong and Petit's law holds reasonably well for most solids at ordinary temperatures and above, but it fails badly at low temperatures, since the specific heat tends towards zero as the temperature approaches 0°K ; it is necessary to apply the principles of quantum theory to explain this behaviour.

In general, the total number of modes of vibration (per gram atom) is equal to $3N$. Thus, if $n(\nu) d\nu$ is the number of modes in the frequency range ν to $\nu + d\nu$,

$$\int_0^{\nu_m} n(\nu) d\nu = 3N \quad (3.2)$$

where ν_m is the maximum frequency. Furthermore, the lattice vibrations obey Bose-Einstein statistics (for which there is no

exclusion principle) so that the average energy in a mode at a frequency ν is $h\nu/\{\exp(h\nu/kT)-1\}$. The internal energy, is, therefore, given by

$$U = \int_0^{\nu_m} \frac{n(\nu)h\nu}{\exp(h\nu/kT) - 1} d\nu. \quad (3.3)$$

Thus, in order to calculate the specific heat due to the lattice vibrations one must know the distribution of normal modes with frequency (i.e. the vibrational spectrum).

The simplest quantum theory of the specific heat was given by Einstein, who assumed that all the vibrational modes have the same frequency ν_E . This assumption leads to an internal energy,

$$U = 3N h \nu_E \left/ \left\{ \exp\left(\frac{h\nu_E}{kT}\right) - 1 \right\} \right., \quad (3.4)$$

and a specific heat per gram atom,

$$C_v = 3Nk(h\nu_E/kT)^2 \exp(h\nu_E/kT) \left/ \left\{ \exp\left(\frac{h\nu_E}{kT}\right) - 1 \right\}^2 \right.. \quad (3.5)$$

The Einstein model explains the fact that the specific heat vanishes at 0°K and, because the total number of modes is $3N$, it is consistent with the high temperature behaviour; however, the temperature-variation of specific heat at low temperatures is not explained.

It is worth mentioning that Nernst and Lindemann modified Einstein's model empirically by assuming that half the modes have a frequency ν_E while the other half have a frequency $\nu_E/2$. This assumption leads to quite good agreement with the experimental results, a fact that ought to be explained by the correct theory.

Debye assumed that a crystalline solid can be represented by an isotropic elastic continuum. The atomic nature of a real solid

is taken into account by limiting the frequency to the maximum value given by Equation (3.2). The solid is supposed to be of some convenient shape, and boundary conditions are applied such that the standing wave associated with each vibrational mode has an integral number of nodal planes in any direction. The situation is similar to that which limits the number of standing wave forms that are permissible in a string that is stretched between two points. Thus, it is found that the number of modes in a given frequency range is given by

$$n(\nu) d\nu = 4\pi V(1/v_l^3 + 2/v_t^3)\nu^2 d\nu \quad (3.6)$$

where V is the volume and v_l and v_t are the velocities of sound waves, with longitudinal and transverse polarization, there being twice as many transverse modes as longitudinal modes. By integrating Equation (3.6) and applying the condition (3.2), it is found that

$$1/v_l^3 + 2/v_t^3 = (9N/4\pi V)/v_m^3. \quad (3.7)$$

Thus, the Debye theory leads to an internal energy

$$U = \frac{9N}{v_m^3} \int_0^{\nu_m} \frac{h\nu^3}{\exp\left(\frac{h\nu}{kT}\right) - 1} d\nu \quad (3.8)$$

and a specific heat per gram atom

$$C_v = \frac{9N}{v_m^3} \int_0^{\nu_m} \frac{h^2\nu^4}{\left\{\exp\left(\frac{h\nu}{kT}\right) - 1\right\}^2} d\nu \quad (3.9)$$

Equation (3.9) can be written in the form

$$C_v = 9Nk(T/\theta_D)^3 F_D(\theta_D/T), \quad (3.10)$$

where θ_D , equal to $h\nu_m/k$, is known as the Debye temperature and $F_D(\theta_D/T)$, the Debye function, is given by

$$F_D\left(\frac{\theta_D}{T}\right) = \int_0^{\theta_D/T} \frac{\left(\frac{h\nu}{kT}\right)^4 \exp\left(\frac{h\nu}{kT}\right)}{\left\{\exp\left(\frac{h\nu}{kT}\right) - 1\right\}^2} d\left(\frac{h\nu}{kT}\right) \quad (3.11)$$

At very low temperatures ($T < \theta_D/12$), the Debye theory predicts that

$$C_v \simeq (12\pi^4 Nk/5) (T/\theta_D)^3 \quad (3.12)$$

so that in this temperature range the specific heat should vary as the cube of the temperature. Figure 10 shows schematically

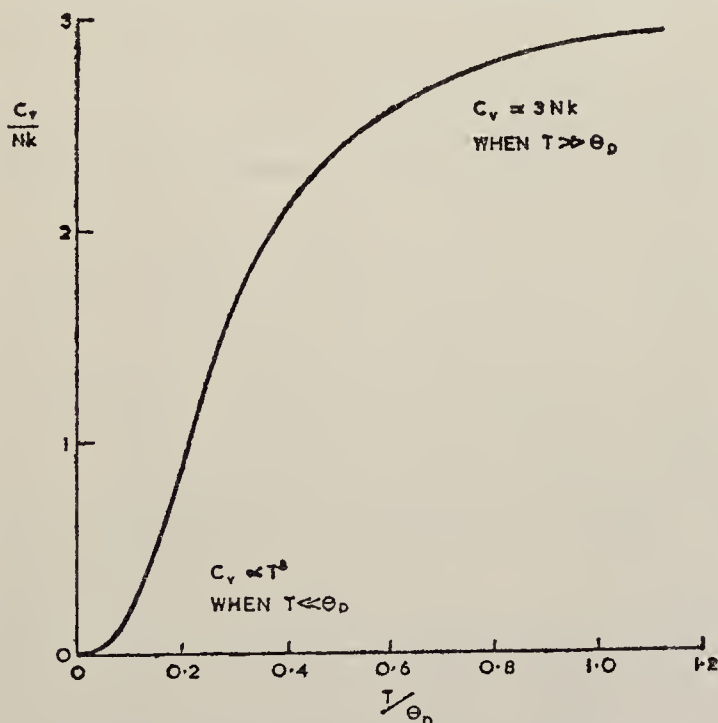


FIG. 10. Variation with temperature of the specific heat per gram atom according to P. Debye's theory.

how the specific heat varies with temperature according to the Debye theory.

Debye's expression for the variation with temperature of the specific heat agrees quite well with the experimental results, but the variation as T^3 is observed only when the temperature is reduced below $\theta_D/50$ rather than $\theta_D/12$. This might be regarded as a trivial point suggesting some minor modification to the Debye vibrational spectrum. However, it must be remembered that even Einstein's crude theory yielded a formula (Equation (3.5)) for the specific heat that is not wildly inaccurate. Thus, it is found that the small degree of disagreement between the experimental data and the Debye theory indicates a large error in the form of the vibrational spectrum. Debye's assumption of an elastic continuum is, in fact, valid for the vibrational modes of very long wavelength but is not justified for the modes of short wavelength and high frequency.

It is useful to compare the propagation of vibrational waves in different media. For the Debye continuum the velocity of

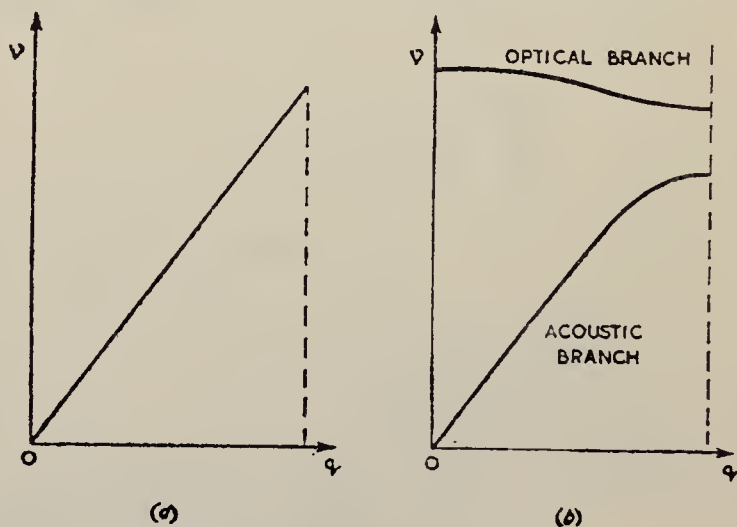


FIG. 11. Dispersion curves for (a) the Debye continuum and (b) a diatomic linear chain.

sound (for a given polarization) is independent of the frequency. This corresponds to the fact that the plot of frequency ν against wavelength q (the dispersion curve) is a straight line as shown in Figure 11(a). The atomic nature of a real crystal lattice affects the dispersion curve, particularly at the higher frequencies. Thus, near the upper frequency limit, the frequency changes only very slowly with wavenumber. If there is more than one atom per unit cell, one can distinguish quite different behaviour between the so-called acoustic and optical modes of vibration. In the acoustic modes, neighbouring atoms tend to be moving in the same direction, whereas in the optical modes they tend to move in opposite directions. Figure 11(b) shows the dispersion curves for the acoustic and optical branches of a one-dimensional lattice having alternate atoms of different mass. It will be seen that, in such a situation, the phase velocity, which is given by $2\pi\nu/q$, is quite different from the group velocity, given by $2\pi d\nu/dq$, i.e. 2π times the slope of the dispersion curve. In a 3-dimensional lattice which has n atoms per unit cell there will be 3 acoustic branches and $(3n - 3)$ optical branches.

Some idea of the real vibrational spectrum of a 3-dimensional crystal was obtained by Blackman. His analysis applied to hypothetical simple-cubic crystal with force constants α_1 and α_2 between nearest-neighbour atoms and next-nearest-neighbour atoms respectively, α_2/α_1 being arbitrarily chosen as 0.05. In Figure 12 the vibrational spectrum obtained by Blackman is compared with that for the Debye model. The double-peak in Blackman's curve (and in many real vibrational spectra) explains the comparative success of the empirical Nernst-Lindemann theory.

In spite of the fact that the Debye theory is now known to be hopelessly inadequate, it is still common practice to express specific heat data in terms of the Debye temperature θ_D . However, in order to account for the departures from the Debye theory, it is supposed that the Debye temperature is temperature-

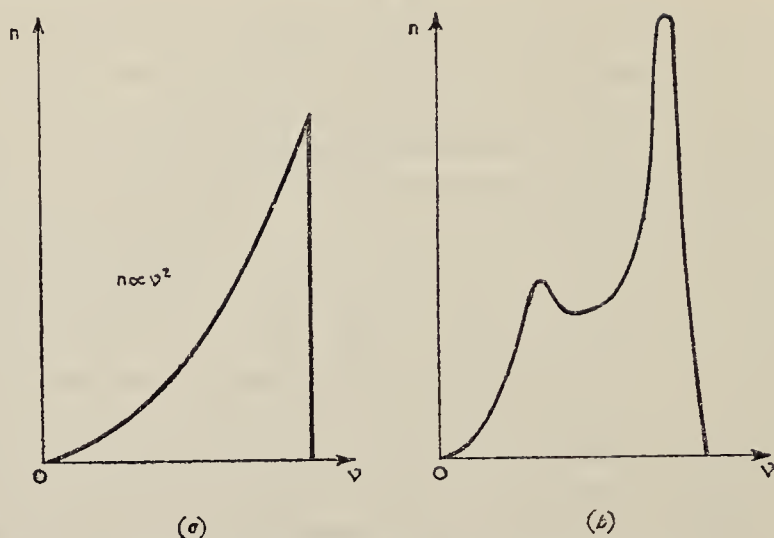


FIG. 12. Vibrational spectra for (a) the Debye continuum and (b) M. Blackman's hypothetical simple cubic crystal.

dependent. The variation of θ_D with temperature for the Blackman simple-cubic lattice is shown in Figure 13.

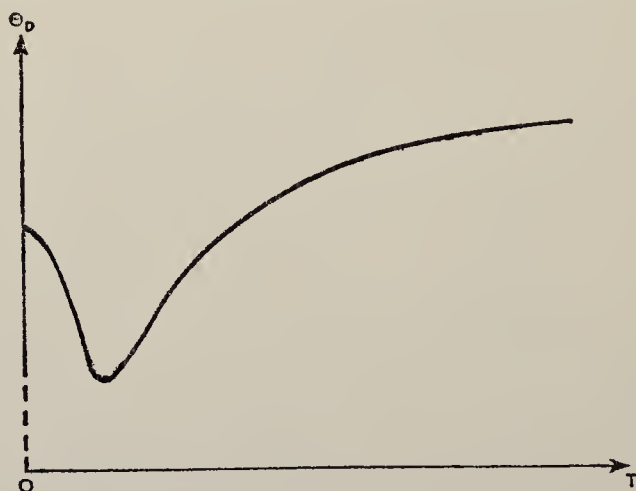


FIG. 13. Variation with temperature of the Debye temperature for Blackman's simple cubic model.

An analysis of specific heat data is of little use in the determination of the vibrational spectrum, since, as has already been pointed out, the temperature-variation of the specific heat is very insensitive to the details of the spectrum. In recent years, a powerful neutron-scattering technique has been applied to the problem. Low-energy neutrons are particularly suitable for the study of vibrational spectra since they are comparable with the phonons in both energy and wavenumber.

3.2. Thermal Expansion

If the thermal vibrations of the lattice were perfectly harmonic, or, in other words, if the interatomic forces obeyed Hooke's law exactly, there would be no change of dimensions of a body on raising its temperature. However, the vibrations in any real solid are to some extent anharmonic, and this leads to the phenomenon of thermal expansion.

Thermal expansion can be explained qualitatively in terms of the schematic plot of potential energy against interatomic spacing shown in Figure 14. At the absolute zero, of course, the lattice has the spacing that corresponds to the lowest potential energy. It would retain this spacing with rise of temperature if the potential energy plot were symmetrical about its minimum, but, in fact, the potential energy rises much more rapidly when the interatomic spacing is reduced than when it is increased. Thus, when the amplitude of the vibrations becomes appreciable, it is energetically favourable for the mean interatomic distance to rise above its value at 0°K.

When the displacement x of the atoms from their spacing at 0°K is kept small the potential energy W may be written as

$$W = ax^2 - bx^3 \quad (3.13)$$

where the term in x^3 represents the asymmetry of the potential energy plot and a and b are constants. Making use of the classical

distribution function, the average displacement \bar{x} is given by

$$\bar{x} = \int_0^{\infty} x \exp(-W/kT) dx \bigg/ \int_0^{\infty} \exp(-W/kT) dx. \quad (3.14)$$

It can be shown from Equation (3.13) that

$$\int_0^{\infty} x \exp(-W/kT) dx \simeq (3\pi^{1/2}/4) \{b(kT)^{3/2}/a^{5/2}\} \quad (3.15)$$

and

$$\int_0^{\infty} \exp(-W/kT) dx \simeq (\pi kT/a)^{1/2} \quad (3.16)$$

Substituting these expressions into Equation (3.14),

$$\bar{x} = (3/4) (bkT/a^2) \quad (3.17)$$

Equation (3.17) suggests that the linear expansion coefficient β , (equal to $d\bar{x}/dT$) should be constant.

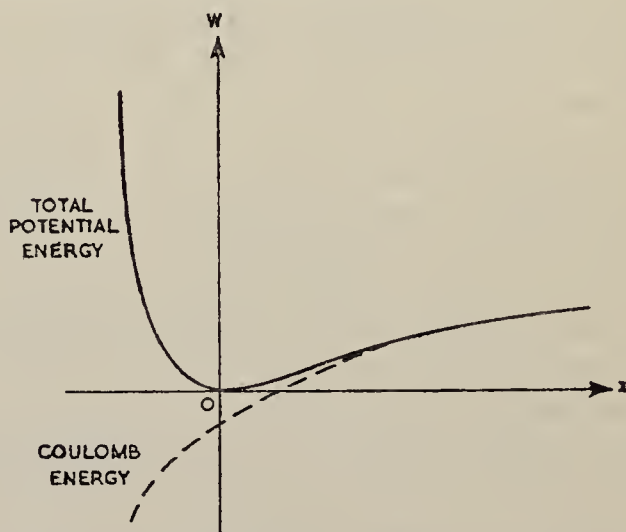


FIG. 14. Schematic variation of potential energy with interatomic spacing. W and x are supposed to have zero values for the equilibrium spacing at 0°K .

The use of the classical distribution function is not expected to be valid at very low temperatures. However, Equation (3.17) can be modified so as to comply with the requirements of quantum statistics if the classical energy kT of a vibrational mode is replaced by $h\nu/\{\exp(h\nu/kT) - 1\}$. This yields

$$\bar{x} = 3bh\nu/4a^2\{\exp(h\nu/kT) - 1\}. \quad (3.18)$$

Equation (3.18) shows that the expansion coefficient should tend towards zero as the temperature approaches 0°K ; this is in agreement with experiment, and complies with the third law of thermodynamics.

Grüneisen observed that the ratio of the expansion coefficient to the specific heat is constant for a given solid at all temperatures. This observation provides a test for the validity of any equation of state for solids. By using the assumptions that are implicit in his theory of the specific heat, Debye was able to show that

$$p = -(\partial U_0/\partial V) + \gamma(U/V) \quad (3.19)$$

where p is the pressure, V is the volume and U is the internal energy which has the value U_0 at 0°K . γ is the Grüneisen parameter which is defined by the equation

$$\gamma = -d(\log \theta_D)/d(\log V) = -(V/\theta_D)(d\theta_D/dV). \quad (3.20)$$

Equation (3.19) is known as the Debye equation of state.

On differentiation, Equation (3.19) yields

$$(\partial p/\partial T)_v = \gamma(C_v/V) \quad (3.21)$$

Also the linear expansion coefficient may be expressed as

$$\beta = (1/3V)(\partial V/\partial T)_p = -(1/3V)(\partial p/\partial T)_v/(\partial p/\partial V)_T. \quad (3.22)$$

Thus, combining Equations (3.21) and (3.22)

$$\beta = \chi\gamma C_v/3V, \quad (3.23)$$

where χ is the compressibility. If the Grüneisen parameter γ is

independent of temperature, β is proportional to C_v in accordance with the Grüneisen law. In typical solids γ has a value of the order of 2.

3.3. Lattice Thermal Conductivity

In 1911 Eucken pointed out that the thermal conductivity of an electrically insulating crystal is inversely proportional to the absolute temperature. Since that time, the Eucken $1/T$ law has been confirmed, at least approximately, for a very large number of crystalline solids at high temperatures. In this context, high temperatures are understood to be those that are greater than the Debye temperature (in fact, Eucken's law seems to hold down to temperatures that are appreciably less than the Debye temperature for many materials).

The $1/T$ law is a clear indication that the resistance to the flow of heat in a solid is provided by the interaction between the various modes of vibration, i.e. by phonon-phonon scattering. As the temperature is raised, the amplitude of the vibrations increases and it is reasonable to suppose that this leads to enhanced scattering. Also, it is known that hard solids like diamond, with high melting points, have larger thermal conductivities than solids which are composed of loosely-bonded atoms; at a given temperature, the effective amplitude of vibration is much less for the strongly-bonded diamond-like materials.

Debye attempted to apply his continuum model, which had been so successful in explaining the behaviour of the specific heat, to the problem of thermal conductivity. However, he found that the thermal conductivity would be infinite if the lattice vibrations were perfectly harmonic, assuming the crystal to be unbounded and free from defects. Thus, anharmonicity is needed to explain the finite thermal conductivity, as well as the thermal expansion, of a real material.

In general, the scattering of a phonon becomes possible only if it encounters a region of the crystal in which the properties that determine its propagation have values that differ from the macroscopic average. In particular, scattering can be due to local changes of either the density or the elastic moduli. The anharmonicity of the lattice vibrations implies that the elastic moduli are dependent on the atomic displacements and, therefore, that they vary throughout the solid.

A notable advance in the theory of lattice thermal conductivity was made by Peierls. He showed that there are two types of interaction between phonons. There are the 'normal' processes in which the momentum of the phonons is conserved, and there are the so-called 'umklapp' processes in which momentum is not conserved, though energy is conserved in both types of process. Peierls showed that the normal processes do not lead directly to any thermal resistance whatsoever, and that it is the 'umklapp' processes that limit the thermal conductivity; his theory is consistent with the observed $1/T$ law of Eucken when $T > \theta_D$.

It can be shown that 'umklapp' processes occur only if two interacting phonons have wavenumbers that, together, exceed the maximum wavenumber in the phonon spectrum. Thus, for the Debye model, the sum of the frequencies of the two phonons should exceed the Debye limiting frequency ν_m . This implies that, at very low temperatures, each of the phonons should have a frequency of about $\nu_m/2$. Now the number of such phonons is approximately proportional to $\exp(-\theta_D/2T)$, whence the phonon mean free path at low temperatures is proportional to $\exp(\theta_D/2T)$. For a more realistic vibrational spectrum the same considerations apply, but it is more generally correct to set the phonon mean free path as proportional to $\exp(\theta_D/bT)$ where b is some numerical constant. By analogy with the kinetic theory of gases, it can be shown that

$$\kappa_L = c_v \rho v_l^2 / 3 \quad (3.24)$$

where κ_L is the lattice thermal conductivity, $c_v\rho$ is the specific heat per unit volume, v is the velocity of sound and l_t is the mean free path of phonons. Thus, when $T \ll \theta_D$, and the specific heat is proportional to T^3 ,

$$\kappa_L \propto T^3 \exp(\theta_D/bT) \quad (3.25)$$

More generally,

$$\kappa_L = \kappa_0 F(\theta_D/T) \quad (3.26)$$

where $F(\theta_D/T) \simeq (T/\theta_D)^3 \exp(\theta_D/bT)$ when $T \ll \theta_D$

and $F(\theta_D/T) \simeq \theta_D/T$ when $T > \theta_D$.

Dugdale and MacDonald have pointed out that the high-temperature lattice thermal conductivity and the expansion coefficient should be related to one another since both quantities depend on departures from Hooke's law. They showed that the relative magnitude of the anharmonicity in different materials can be represented by a dimensionless parameter equal to $\beta\gamma T$, where β and γ are the linear expansion coefficient and the Grüneisen parameter respectively. They then supposed that the phonon freepath length l_t is approximately equal to the lattice constant a divided by this dimensionless parameter. Thus,

$$l_t \simeq a/\beta\gamma T. \quad (3.27)$$

Substituting in Equations (3.24) and (3.26) for $T > \theta_D$,

$$\kappa_0 \simeq c_v\rho va/3\beta\gamma\theta_D. \quad (3.28)$$

Furthermore, making use of the Grüneisen equation (3.23) to eliminate β , and using the Debye relation between the velocity of sound, the compressibility and the Debye temperature,

$$\kappa_0 \simeq 8(k/h)^3(a^4\rho\theta_D^2/\gamma^2) \quad (3.29)$$

This equation, when combined with Equation (3.26), allows the lattice thermal conductivity of a crystal to be predicted,

and it shows that materials with high Debye temperatures usually have large thermal conductivities.

Peierls' prediction that the lattice thermal conductivity of a pure crystal should vary with temperature according to an exponential law when $T \ll \theta_D$, directed attention towards the low temperature region, where much of the most interesting work has since been carried out. It was found that the thermal conductivity does not rise without limit as the temperature is lowered, but reaches a maximum value, usually at about one-twentieth of the Debye temperature. At still lower temperatures the thermal conductivity of a pure crystal is proportional to T^3 . Bearing in mind the fact that the specific heat in this region is also proportional to T^3 , this indicates that the mean free path of the phonons has reached a constant value. Casimir pointed out that this constant free path length is of the same order as the dimensions of the specimen if it is a single crystal, or of the grain size if the material is polycrystalline. It is clear that the scattering of the phonons occurs at the crystal boundaries under these conditions.

It is perhaps unrealistic to extend the concept of phonons to amorphous solids but the above ideas can be of some use even for these materials. It turns out that the apparent 'phonon' free path length as derived from Equation (3.24) is of the order of the interatomic spacing for an amorphous substance.

The thermal conductivity of most materials at low temperatures falls some way short of the value to be expected if scattering of phonons were due solely to the thermal vibrations and the crystal boundaries. This is, of course, because of the additional scattering of phonons by various imperfections in the lattice, which, in general, alter both the local elastic properties and the local density. If the disturbed region extends over a distance that is appreciably less than the phonon wavelength, the Rayleigh scattering theory is applicable and the scattering cross-section of each point defect varies as $c^6 q^4 (\Delta\chi/\chi + \Delta\rho/\rho)^2$,

where c is the linear dimension of the defect, q is the phonon wavenumber, $\Delta\chi$ is the change in compressibility from the average value χ and $\Delta\rho$ is the change in density from the average value ρ .

There is not much difficulty in applying the Rayleigh scattering formula to calculate the thermal resistance due to 'point' defects at high temperatures. Since 'point' defects are particularly effective in scattering phonons of short wavelength, these phonons cannot carry much heat, and it does not really matter that the Rayleigh formula can be applied strictly only when $c \ll \lambda$, where λ is the phonon wavelength. It is, however, rather more difficult to calculate the thermal conductivity at low temperatures if point-defect scattering is predominant.

The difficulty at low temperatures arises from the fact that 'point' defects scatter the long-wavelength phonons very weakly. Thus, at temperatures which are so low that 'umklapp' scattering is negligible, it might seem that the crystal boundaries provide the only mechanism for scattering the phonons of long wavelength. On the other hand, the measured thermal conductivities of impure crystals are size-independent and too small for boundary scattering to be important. The explanation of this paradox is to be found if the normal processes are taken into account. Although these processes do not lead directly to any thermal resistance, they redistribute momentum between the phonon modes. Thus, the momentum in the long-wavelength modes can be transferred to the short-wavelength modes by the normal processes and, once it is in the short wavelength modes, it can be removed effectively by 'point'-defect scattering.

Point defects are, of course, most effective as scatterers of phonons if they give rise to intense local variations of both the interatomic forces and the density. However, even the density fluctuations that arise from the differences between the atomic weights of the isotopes in naturally-occurring elements, can lead to a substantial reduction in the phonon free path length of an

otherwise pure crystal. For example, a substantial increase in the thermal conductivity of germanium on enriching the Ge^{74} content at the expense of the other isotopes has been observed. Ordinary germanium contains five isotopes with concentrations ranging from about 7% to 37%; the enriched material contained 96% of Ge^{74} and less than 2% of any of the other iso-

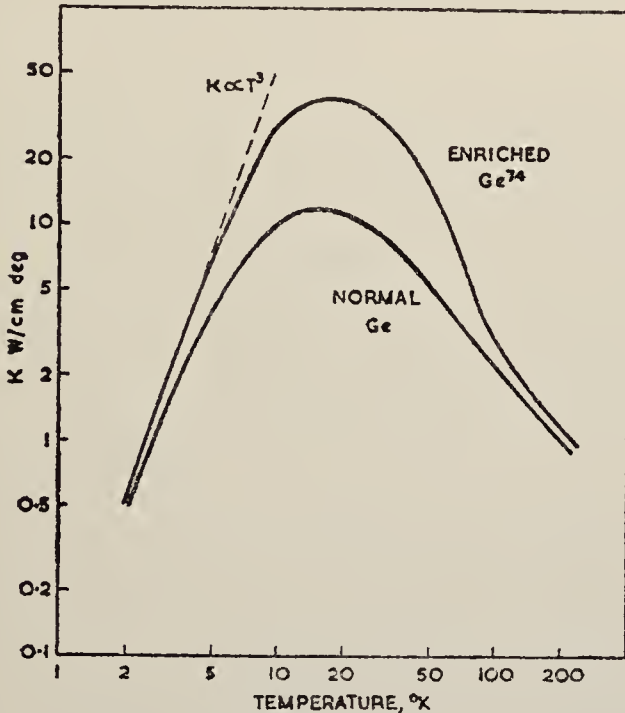


FIG. 15. Variation with temperature of the thermal conductivity of a crystal of ordinary germanium compared with that of a crystal in which the isotope Ge^{74} has been considerably enriched (according to T. H. Geballe and G. W. Hull).

topes. The experimental results are shown in Figure 15. It should be noted that, although germanium is a semiconductor, the electronic contribution to the thermal conductivity is negligible except at high temperatures.

Phonons can be scattered by 'line' defects (i.e. dislocations) as well as 'point' defects. The core of a dislocation should lead to Rayleigh-type scattering but, in fact, it is found that the scattering due to the strained region of crystal in the neighbourhood of a dislocation is rather more important. The measurement of the thermal resistivity of a strained crystal can be utilised in estimating the density of dislocations in the material.

4 The Specific Heat and Thermal Conductivity of Metals

4.1. Heat Capacity of the Electrons

It has already been pointed out that the specific heat of a metal at high temperatures obeys the Dulong and Petit law, the electronic contribution to the heat capacity being negligible. The conduction electrons do have an indirect effect on the specific heat at intermediate temperatures (T not much less than θ_D) through their influence on the vibrational spectrum, since they are responsible for the binding of the atoms in a metal. At very low temperatures, however, the electronic specific heat of a metal can exceed the lattice specific heat, though both contributions are rather small.

The discussion in Section 2.2, shows that, at a temperature T , the number of electrons that occupy energy states (which would be empty at the absolute zero of temperature) is approximately proportional to kT/ζ . An electron in one of these excited states will have increased its energy by about kT , so that the electronic contribution to the internal energy is proportional to k^2T^2/ζ ; the specific heat of the electrons is then proportional to T . Since the lattice specific heat at very low temperatures is proportional to T^3 , the total specific heat can be written in the form

$$c_v = AT^3 + BT, \quad (4.1)$$

where the constants A and B depend on the lattice and the electrons respectively. A plot of c_v/T against T^2 should be a straight line of slope A intercepting the ordinate axis at B . Such

a plot, therefore, allows the relative contributions to the specific heat of the lattice and the electrons to be found.

The electronic specific heat may be calculated from the free-electron quantum theory using Equations (2.1) and (2.2). The mean energy per electron is

$$\bar{\varepsilon} = \frac{\int_0^{\infty} \varepsilon g(\varepsilon) f(\varepsilon) d\varepsilon}{\int_0^{\infty} g(\varepsilon) f(\varepsilon) d\varepsilon}. \quad (4.2)$$

Using the 'degenerate' approximations, for $\zeta \gg kT$, it can be shown that the internal energy of the n electrons per unit volume is

$$n\bar{\varepsilon} \simeq u_0 + \frac{\pi^2}{6} (kT)^2 g(\zeta_0), \quad (4.3)$$

where u_0 , equal to $3n\zeta_0/5$, is the internal energy at 0°K , and ζ_0 is the Fermi energy at the same temperature. Thus, the specific heat due to the electrons is

$$c_v = \frac{\pi^2}{3} k^2 T g(\zeta_0) \quad (4.4)$$

It is not too surprising that the expression for the electronic specific heat contains as its only variable the density of electronic states at the Fermi level.

It is usual to express the electronic specific heat per mole as

$$C_v = \gamma_e T \quad (4.5)$$

Then, for a free-electron gas it is found that

$$\gamma_e = (4\pi^{5/3}/3^{2/3})(A/\rho)(k^2 m n^{1/3}/h^2) \quad (4.6)$$

where A/ρ is the volume per mole. The value of γ_e for a free-electron gas is about 10^{-3} J/mole deg² whereas the experimental values of γ_e are often very much larger than this. This disagreement can be removed if the free-electron mass m in Equations

(4.6) is replaced by an effective mass m^* so as to take account of the effect on the electrons of the crystal lattice.

One might expect the same value of m^* to be applicable for all the electronic properties of a metal, if the surfaces of constant energy in wavevector-space were spherical (see Section (2.3)). However, even for the monovalent alkali metals, there are differences between the effective masses as found from the specific heat and transport properties.

The values of γ_e for the divalent metals can be much less than, or much greater than, the free-electron value. This is because there is a rapid variation with energy of the density of states near the Fermi level, and the precise value at the Fermi level is particularly sensitive to the electron concentration.

The transition metals are remarkable in that the parameter γ_e displays a similar variation within each of the periods of the periodic table. Particularly noteworthy is the fact that very low values of γ_e are found for the metals chromium, molybdenum and tungsten; each has a total number of six, out of a possible twelve, outer electrons in the overlapping s and d bands. This shows that the density of electronic states has a pronounced minimum at the middle of the 3d, 4d and 5d bands.

Specific heat measurements at low temperatures on the superconducting metals have been most instructive. It is found that the electronic specific heat in the superconducting state is proportional to $\exp(-\text{const.}/T)$. This is a good indication that there is an activation energy associated with the superconducting electrons and provides strong evidence for the existence of an energy gap in accordance with the 'microscopic' theory of superconductivity.

4.2. Electronic Thermal Conductivity

As was mentioned in Section 2.2, the classical free-electron theory provided an explanation of the Wiedemann-Franz law,

but this was due to the fact that both the electrical and thermal conductivities were wrongly estimated by about the same factor. Even closer agreement with the experimentally-determined ratios of κ to σ results from the application of the quantum theory.

The electronic thermal conductivity κ_e can be calculated using an equation similar to Equation (3.24) but with the specific heat, velocity and free path length of the phonons replaced by the same properties of the electrons. The mean velocity of the electrons in a metal is $(2\zeta/m)^{\frac{1}{2}}$ so that, using Equations (4.5) and (4.6) for the electronic specific heat, it is found that

$$\kappa_e = (\pi^2/3)nk^2Tl_e/(2m\zeta)^{\frac{1}{2}} \quad (4.7)$$

where l_e is the electronic free path. The electrical conductivity of a metal on the free-electron quantum theory is given by

$$\sigma = ne^2l_e/(2m\zeta)^{\frac{1}{2}} \quad (4.8)$$

whence

$$\kappa_e = (\pi^2/3)(k/e)^2\sigma T. \quad (4.9)$$

The ratio $\kappa_e/\sigma T$ is known as the Lorenz number L and is equal to $(\pi^2/3)(k/e)^2$ for a degenerate electron gas. The value of the Lorenz number remains the same if the free-electron theory is replaced by band theory.

Experimental values for the ratio $\kappa/\sigma T$ for a number of metals are given in Table 2 and in all cases there is good agreement with the theoretical value for the Lorenz number, 2.45×10^{-8} W ohm/deg². It may surprise the reader that the agreement is so good, since it might be expected that the lattice vibrations would also contribute to the thermal conductivity. In fact, for nearly all metals and alloys at ordinary temperatures, the lattice thermal conductivity is found to be negligible. This is because the electronic contribution is so large, and because the scattering of phonons by the conduction electrons tends to make the lattice contribution very small.

TABLE 2. Measured values of $\kappa/\sigma T$ for various metals at 0°C.

Metal	$\kappa/\sigma T \times 10^8$ W ohm/deg ²
Copper	2.23
Silver	2.31
Gold	2.35
Cadmium	2.42
Zinc	2.31
Tungsten	3.04
Molybdenum	2.61
Tin	2.52
Lead	2.47
Platinum	2.51

At low temperatures the Wiedemann-Franz law is no longer strictly applicable. It will be supposed that the electronic thermal resistivity is given by

$$W_e = W_0 + W_t \quad (4.10)$$

where W_0 is the thermal resistivity due to scattering by the impurities and other defects and W_t is that due to scattering by the lattice vibrations. W_0 is given in terms of the electrical resistivity ρ_0 due to the defects (ρ_0 is known as the residual resistivity since it is the resistivity at 0°K) by Equation (4.9). Thus,

$$W_0 = \rho_0 \frac{\pi^2}{3} \left(\frac{k}{e} \right)^2 T. \quad (4.11)$$

On the other hand, W_t is *not* related in the same way to the electrical resistivity ρ_t due to scattering by the lattice vibrations.

When $T \ll \theta_D$, the fact that most of the phonons have a very long wavelength has a marked effect on the scattering of the electrons. It turns out that there is very little change of *momentum* of an electron when it collides with a phonon, so that the electrical resistivity falls very rapidly as the temperature is

lowered; ideally the electrical resistivity at low temperatures should vary as T^5 . However, the transfer of *energy* when an electron collides with a long-wavelength phonon, is rather more effective than the transfer of momentum. Thus, the electronic thermal resistivity does not fall so rapidly as the electrical resistivity with decreasing temperature, since it is energy transfer that is important in the heat conduction process. The low-temperature electronic thermal resistivity is proportional to T^2 so that W_t/ρ_t is proportional to T^{-3} , whereas at ordinary temperatures this ratio varies as T^{-1} .

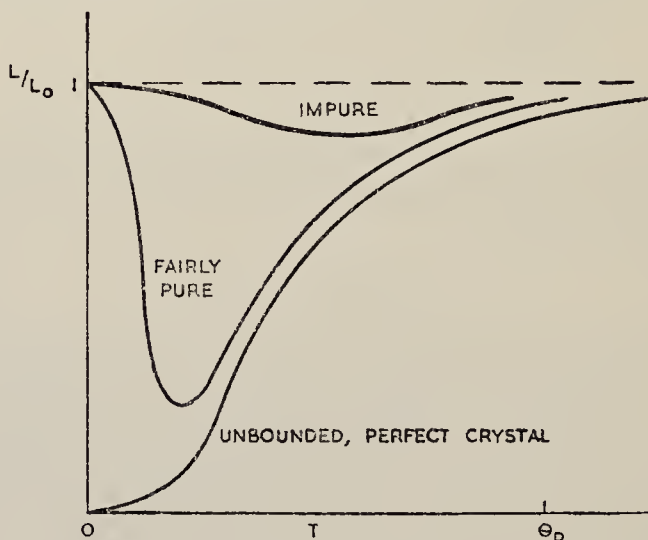


FIG. 16. Schematic variation of Lorenz number with temperature for a metal in the pure and impure state. L_0 is the high-temperature Lorenz number given by Equation (4.11).

Figure 16 shows schematically how the Lorenz number is expected to vary with temperature for a metal when it is pure and when it is impure. If there were no imperfections whatsoever in an unbounded crystal, the Lorenz number would tend towards zero as the temperature approached 0°K . However, for any real crystal, scattering of the electrons by imperfections becomes

predominant at the lowest temperature, so that, in accordance with Equation (4.11), the Lorenz number returns to the high temperature value L_0 . For a fairly pure crystal, the Lorenz number can have a minimum value about an order of magnitude less than L_0 , whereas an impure sample may well retain a Lorenz number close to L_0 at all temperatures.

Interesting results are obtained from thermal conductivity measurements on superconductors, since superconducting electrons do not take part in the conduction of heat. Thus, the thermal conductivity of a pure metal becomes smaller when it changes from the normal to the superconducting state. On the other hand, the thermal conductivity of an alloy can rise on its transition into the superconducting state. This is because the lattice thermal conductivity may not be negligible in comparison with the electronic thermal conductivity for an alloy; thus, the increase in the lattice thermal conductivity, due to the reduction of phonon-scattering by the electrons, may more than compensate for the fall in the electronic thermal conductivity when the alloy becomes superconducting.

5 Thermal Effects in Semiconductors

5.1. The Thermoelectric Effects

It is unnecessary to derive independent expressions for the three thermoelectric coefficients, since they are related to one another by Kelvin's laws, Equations (1.5) and (1.6). Probably it is simplest to explain the origin of the Peltier coefficient which, as defined in Section 1.5, is a measure of the energy transported by the charge carriers.

To a first approximation, the differential Peltier coefficient between any two metals is zero since the mobile electrons all occupy states that have energies close to the Fermi energy ζ . The small Peltier effects actually observed between different metals can be explained in terms of the details of the energy bands, the Fermi energy and the scattering mechanisms. Here we are interested in the much larger Peltier effects that are observed when at least one of the conductors at the junction is a non-degenerate semiconductor.

It will be supposed that the semiconductor is *n*-type and that it forms a junction with a metal, It is assumed that the metal has zero absolute thermoelectric coefficients, which implies that the energy states of the mobile electrons coincide, on the average, with the Fermi level of energy. Figure 17 is the energy diagram for the junction; at equilibrium the Fermi level must be the same in both substances. It will be seen that the Fermi energy ζ , as measured from the bottom of the conduction band, is a negative quantity for the semiconductor. When a positive current of electricity flows from right to left, each electron

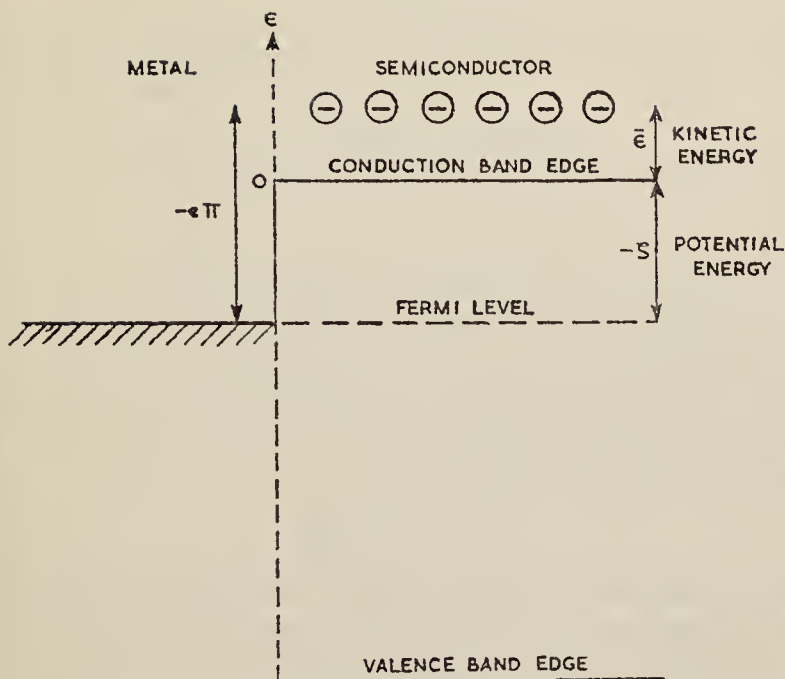


FIG. 17. Energy diagram for a junction between a metal and an *n*-type semiconductor illustrating the origin of the Peltier effect.

(travelling in the opposite direction) must absorb an amount of energy $-\zeta$ at the junction in order to reach the edge of the conduction band of the semiconductor. Moreover, in the semiconductor, the electrons which carry the current have a certain mean kinetic energy $\bar{\epsilon}$ so that the total energy change at the junction is $(\bar{\epsilon} - \zeta)^*$. Now the Peltier coefficient is defined as the mean energy transported per unit charge. Thus, for the semiconductor

$$\pi = -\frac{\bar{\epsilon} - \zeta}{e} \quad (5.1)$$

*Here $\bar{\epsilon}$ is the average kinetic energy transported by the electrons; the contributions of the electrons of different energy are, therefore, weighted according to the amount of the current which they carry.

where the negative sign has been inserted in accordance with the usual convection. It should be noted that a similar discussion can be applied to a p -type semiconductor, but then the Peltier coefficient has a positive sign, indicating the liberation of heat when a positive current flows from the semiconductor to the metal.

The mean kinetic energy $\bar{\epsilon}$ of the charge carriers depends on the precise form of the density of states distribution function and on the nature of the scattering processes. It is usually legitimate to assume that $g(\epsilon) \propto \epsilon^{\frac{1}{2}}$ for a semiconductor, in accordance with Equation (2.1). Thus, if it is supposed that the mean free path of the charge carriers is proportional to ϵ^s , where s is a constant, it can be shown that

$$\bar{\epsilon} = (s + 2) kT. \quad (5.2)$$

In the simplest situation, s is zero when the carriers are scattered by the acoustic-mode lattice vibrations, and has a value 2 when the scattering is due to ionized impurities. In general, the thermoelectric coefficients are given by

$$\alpha = \frac{\pi}{T} = \mp \frac{k}{e} \left(s + 2 - \frac{\zeta}{kT} \right) \quad (5.3)$$

where the upper and lower signs apply to n -type and p -type materials respectively.*

It is worth mentioning that the Fermi energy ζ of a semiconductor is related to the concentration n of the charge carriers by the equation

$$n = 2 (2\pi m^* kT/h^2)^{\frac{3}{2}} \exp(\zeta/kT) \quad (5.4)$$

*Electrons entering an n -type semiconductor absorb energy as they climb up to the conduction band; when they enter a p -type semiconductor they give up energy as they fall into the valence band. Thus, the Peltier (and Seebeck) coefficients of n - and p -type materials have opposite signs. ζ would be measured downwards from the top of the valence band for a p -type semiconductor.

Thus, a semiconductor with a high carrier concentration and, therefore, a high electrical conductivity, usually has low thermoelectric coefficients, whereas semiconductors with poor electrical conductivities tend to have high thermoelectric coefficients.

The measurement of the Seebeck coefficient of an extrinsic semiconductor provides a means for determining the effective mass of the charge carriers, if it is combined with a measurement of the Hall coefficient to determine the carrier concentration n . If a value for the coefficient s can be assigned (perhaps from the temperature-dependence of the mobility of the charge carriers), Equation (5.3) allows ζ to be found in terms of α so that m^* remains the only unknown quantity in Equation (5.4). The effective mass that is determined from Hall and Seebeck measurements is identical with the effective mass that is found from, say, cyclotron resonance experiments if the surfaces of constant energy are spherical and centred at the origin in wave-vector space.

5.2. Conduction of Heat in Semiconductors

In many semiconductors the carrier concentration is so small that the electronic component of the thermal conductivity is negligible. Studies of heat conduction by the lattice in such materials have been fruitful (particularly because of their availability, in some cases, in the form of large and pure single crystals, as used by the transistor industry).

Measurements on semiconductors with high carrier concentrations are interesting in that these materials can have lattice and electronic components of the thermal conductivity of the same order of magnitude. One is then faced with the problem of separating the two components from one another.

For a non-degenerate semiconductor, the electronic thermal conductivity is given by

$$\kappa_e = (s + 2)(k/e)^2 \sigma T \quad (5.5)$$

where σ is the electrical conductivity and s is the scattering parameter defined in Section 5.1. Equation (5.5) is, however, not usually valid if the electronic thermal conductivity is appreciable compared with the lattice conductivity, since it is then unlikely for the classical condition $\zeta < -2kT$ to be obeyed. Usually the value of κ_e is intermediate between that given by Equation (5.5) and that given by the degenerate relation (4.9); the precise value of the Lorenz number can be determined only by using the complete Fermi-Dirac statistics. If the lattice component is independent of the carrier concentration, the plot of the total thermal conductivity against the electrical conductivity for an extrinsic semiconductor at a given temperature, takes the form shown in Figure 18.

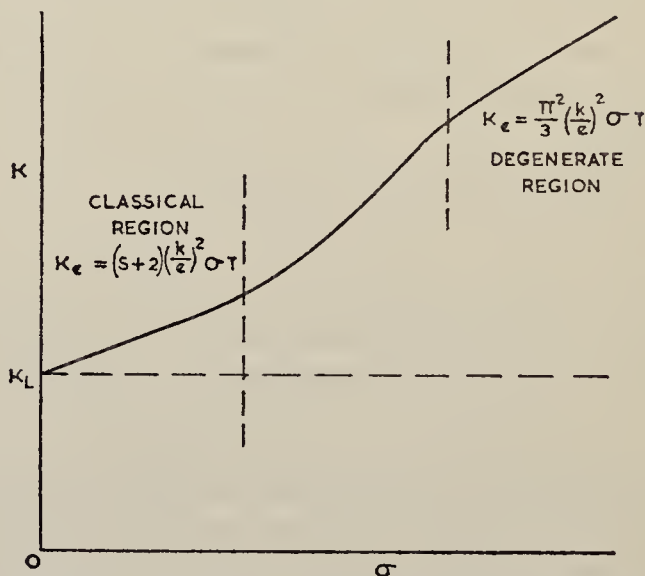


FIG. 18. Schematic plot of thermal conductivity against electrical conductivity for an extrinsic semiconductor at a given temperature. The lattice thermal conductivity is assumed to be constant.

Even if the scattering parameter s is not known, the lattice component of the thermal conductivity can be estimated by

extrapolation to zero electrical conductivity. Generally, however, the lattice thermal conductivity will fall as the electrical conductivity rises, since the impurities used to dope the semiconductor will scatter the phonons. The thermal conductivity of iodine-doped (*n*-type) and lead-doped (*p*-type) bismuth telluride at a temperature of 150°K is plotted against electrical conductivity in Figure 19(a). After subtracting the calculated electronic component from the total thermal conductivity, it is

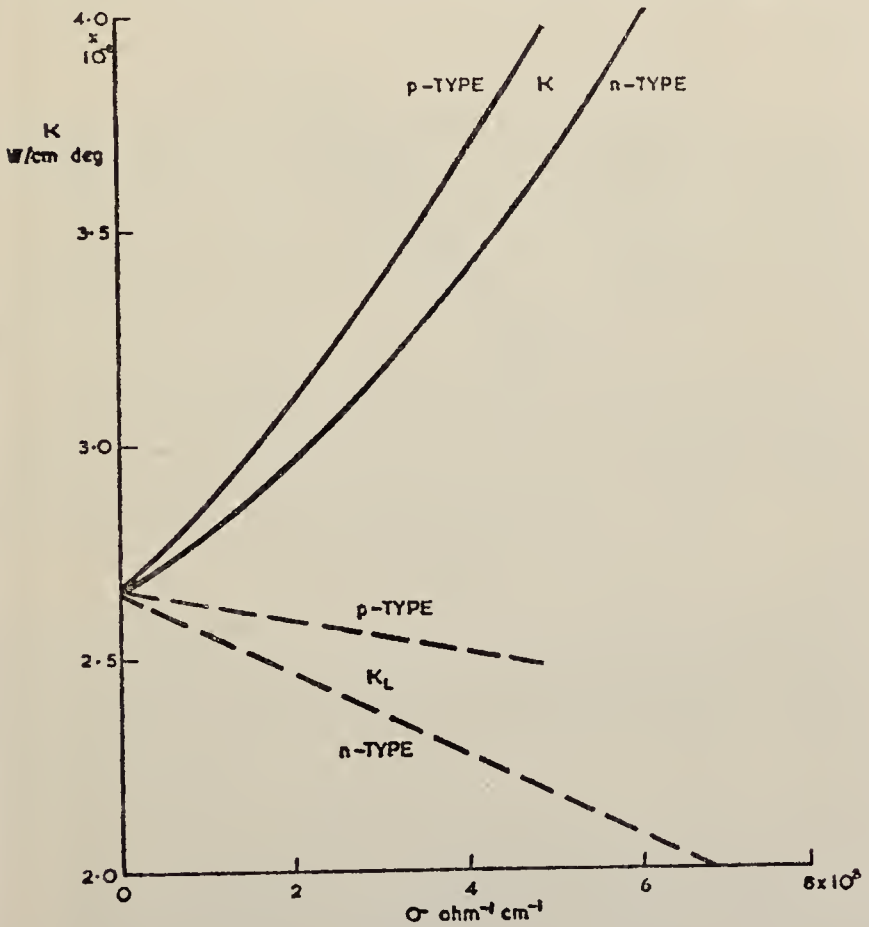


Fig. 19a

found that the lattice component falls with increasing concentration of the doping agent.

Figure 19(b) shows a similar plot for bismuth telluride at 300°K. The most notable feature is the large increase of the

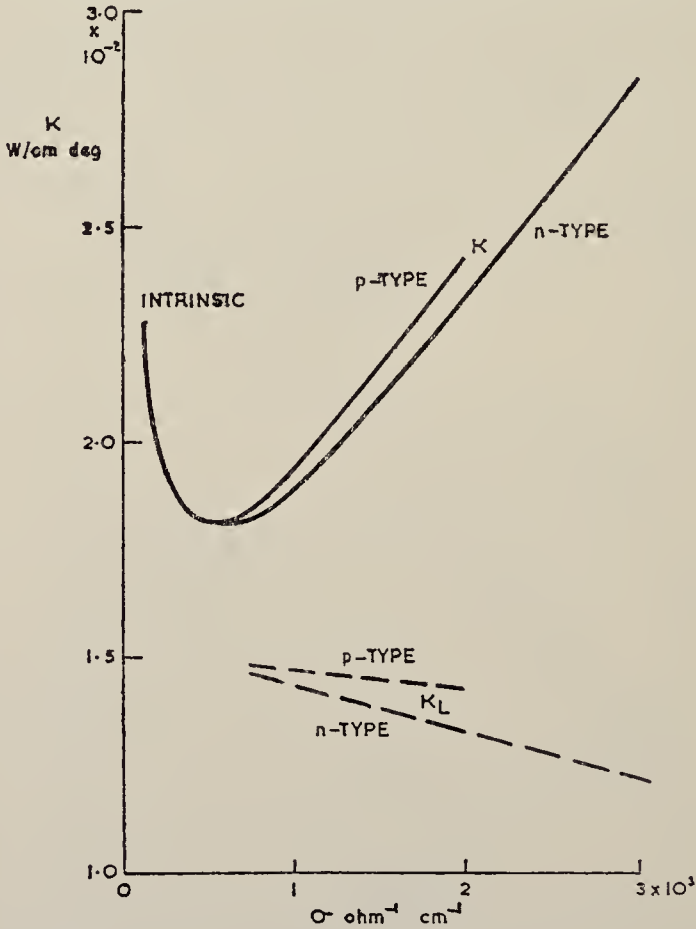


Fig. 19b

FIG. 19. Thermal conductivity plotted against electrical conductivity for bismuth telluride at (a) 150°K and (b) 300°K. The electronic component of the thermal conductivity in the extrinsic region is calculated assuming the scattering parameter s to be equal to zero.

thermal conductivity when the electrical conductivity has its lowest values. This effect is associated with the presence of both electrons and holes in an intrinsic (or near-intrinsic) semiconductor and is known as the 'bipolar' heat-conduction effect.

When an electric field E and a temperature gradient ∇T are applied to a mixed semiconductor there will be electric currents of density i_n and i_p , for the electrons and holes respectively, given by

$$\left. \begin{aligned} i_n &= \sigma_n(E - \alpha_n \nabla T) \\ \text{and } i_p &= \sigma_p(E - \alpha_p \nabla T) \end{aligned} \right\} \quad (5.6)$$

where σ_n and σ_p are the so-called partial electrical conductivities of the two types of carrier and α_n and α_p are the partial Seebeck coefficients, calculated from Equation (5.3) for each energy band separately. Equations (5.6) show immediately that the total electric current density when $\nabla T = 0$ is $(\sigma_n + \sigma_p)E$, so that the total electrical conductivity is merely the sum of the partial conductivities σ_n and σ_p .

The Seebeck coefficient and the thermal conductivity are defined for zero electric current so that $i_n = -i_p$. When this condition is applied to Equation (5.6), remembering that the Seebeck coefficient is defined as $E/\nabla T$, it is found that

$$\alpha = (\alpha_p \sigma_p + \alpha_n \sigma_n) / (\sigma_n + \sigma_p), \quad (5.7)$$

which might have been expected. The total Seebeck coefficient is a weighted average of the partial coefficients for the two types of carrier, which, it will be recalled, are of opposite sign.

The densities of the flows of energy due to the electrons and holes are given by

$$w_n = \alpha_n T i_n - \kappa_n \nabla T \quad (5.8)$$

$$\text{and } w_p = \alpha_p T i_p - \kappa_p \nabla T$$

respectively, where the partial Peltier coefficients have been set

equal to $\alpha_n T$ and $\alpha_p T$ and where κ_n and κ_p are the partial thermal conductivities of the electrons and holes. Thus, equating the overall electronic thermal conductivity κ_e with $-(w_n + w_p)/\nabla T$, it is found that

$$\kappa_e = \kappa_n + \kappa_p + \left\{ \frac{\sigma_n \sigma_p}{\sigma_n + \sigma_p} \right\} (\alpha_p - \alpha_n)^2 T. \quad (5.9)$$

If the semiconductor is non-degenerate $(\kappa_n + \kappa_p)$ is given by $(s+2)(k/e)^2(\sigma_n + \sigma_p)T$. Furthermore, $(\alpha_p - \alpha_n)$ is equal to $(k/e)(\varepsilon_g/kT + 2s + 4)$ since the sum of the Fermi energies for the electrons and holes is equal to $-\varepsilon_g$, where ε_g is the energy gap. Thus, if the concentrations of the two types of carrier are equal,

$$\kappa_e = \left[(s+2) + \left\{ \frac{\mu_n \mu_p}{\mu_n + \mu_p} \right\} (\varepsilon_g/kT + s + 4)^2 \right] (k/e)^2 \sigma T \quad (5.10)$$

where μ_n and μ_p are the mobilities of the electrons and holes.

If s has its usual value of zero, and if μ_n and μ_p are nearly equal, it can be seen that the Lorenz number is changed from $2(k/e)^2$ for an extrinsic sample, to about $\{2 + (\varepsilon_g/2kT + 2)^2\}(k/e)^2$ for an intrinsic one. Bismuth telluride has an energy gap equal to about $6kT$ at room temperature so that the Lorenz number of an intrinsic specimen is no less than about $27(k/e)^2$. It is immediately obvious why the thermal conductivity rises to a high value at low electrical conductivities as shown in Figure 19(b).

5.3. Thermomagnetic Effects in Extrinsic and Intrinsic Semiconductors

When the mean free time between the collisions of the charge carriers increases with their energy, ($s > \frac{1}{2}$), the more energetic electrons make the greater contribution to the transport properties. On the other hand, if the mean free time decreases with increasing energy, ($s < \frac{1}{2}$), the less energetic carriers make the greater contribution. One of the effects of a magnetic field

is that it tends to make the contributions of the charge carriers of different energy more nearly equal. This means that, if $s > \frac{1}{2}$, the Seebeck coefficient falls on the application of a magnetic field, whereas if $s < \frac{1}{2}$ the Seebeck coefficient rises. The sign and magnitude of the magneto-Seebeck effect in an extrinsic semiconductor is, therefore, of some use in determining the scattering law.

The thermal conductivity falls when a magnetic field is applied, the effect being analogous to the fall in electrical conductivity, i.e. the magneto-resistance effect. It is sometimes possible to reduce the electronic thermal conductivity to negligible proportions by applying a strong magnetic field, whence the lattice contribution κ_L can be determined directly.

Since the Ettingshausen and Nernst effects are related to one another by Equation (1.8), it is unnecessary to discuss them independently. Thus, we consider specifically how the Ettingshausen effect arises, though, in practice, it is easier to measure the Nernst coefficient than the Ettingshausen coefficient.

The origin of the Ettingshausen effect in an extrinsic n -type semiconductor is illustrated in Figure 20(a). It is supposed that an electric current flows from left to right so that, when a magnetic field is applied in the direction away from the reader, the Lorentz force tends to drive the electrons upwards. No net flow of current is, however, permissible, as an electric field (the Hall field) is built up and, at equilibrium, the force due to this field, on the average, exactly balances the Lorentz force. In fact, if all the electrons possessed the same energy, there would be no transverse flow whatsoever. In general, however, (if $s \neq \frac{1}{2}$) there is a tendency for the electrons of different energy to behave in different ways. If, for example, the more energetic electrons are the more strongly scattered ($s < \frac{1}{2}$, as shown in the diagram) these electrons tend to drift downwards under the action of the Hall field, whereas the less energetic electrons tend to drift upwards due to the Lorentz force. Although the overall

THERMAL EFFECTS IN SEMICONDUCTORS

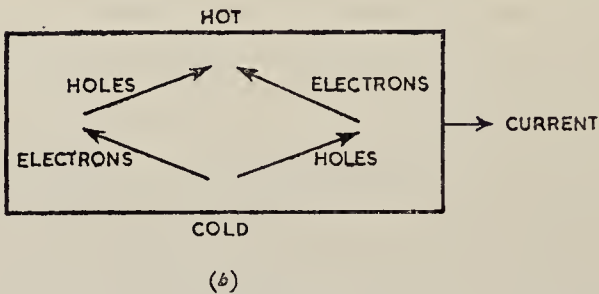
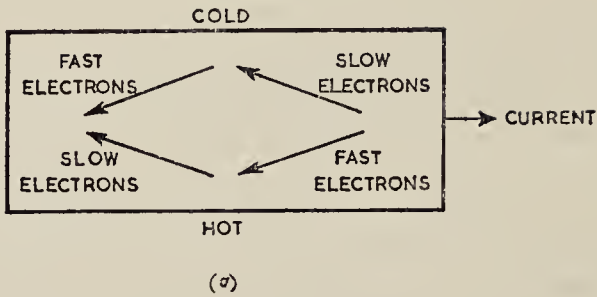


FIG. 20. Origin of the Ettingshausen effect in (a) an extrinsic *n*-type semiconductor and (b) an intrinsic conductor. In case (a) it is supposed that the scattering is more intense for the high energy electrons. The magnetic field is directed away from the reader.

transverse flow of charge must remain zero, there is a flow of heat (in the direction of drift of the more energetic electrons) which continues until an equilibrium temperature gradient is built up. The direction of the transverse temperature gradient indicates whether s is greater than or less than $\frac{1}{2}$, and the ratio of the Nernst or Ettingshausen coefficient to the Hall coefficient gives the precise value of s .

If the above discussion is applied to a *p*-type semiconductor it is found that the direction of the transverse temperature gradient is unaltered. It is apparent that the sign of the Nernst or Ettingshausen coefficient does not depend on the sign of the

charge carriers. On the other hand, the Righi-Leduc coefficient, like the Hall and Seebeck coefficients, always has the same sign as that of the charge carriers.

Figure 20(b) shows the origin of the Ettingshausen effect in an intrinsic conductor. Although the longitudinal flows of electrons and holes are in opposite directions, the Lorentz force tends to produce transverse flows of both types of carrier in the same direction. It will be appreciated that equal flows of electrons and holes in the same transverse direction are permissible since they do not lead to any net current flow. The bipolar Ettingshausen effect tends to be much larger than the Ettingshausen effect in an extrinsic semiconductor because (1) the transverse motion of the charge carriers is not impeded by a large Hall field* and (2) the electrons and holes transport their ionization energy as well as their kinetic energy. Furthermore, the Ettingshausen coefficient in intrinsic material remains more or less constant as the magnetic field rises, whereas it falls to zero for an extrinsic conductor in a high field. Such characteristics of the Ettingshausen effect in intrinsic conductors (particularly low-energy gap semiconductors and semi-metals) make possible its effective use in refrigeration.

5.4. Phonon Drag

So far it has been assumed implicitly that the transport of charge and heat by the electrons and holes is independent of heat transport by the phonons. This assumption is usually perfectly valid, but in certain materials, particularly at low temperatures, it breaks down. The effects that arise from the inter-dependence of the flows of electrons and phonons are known as the phonon drag effects.

*The Hall coefficient is equal to zero in an intrinsic conductor if the electron and hole mobilities μ_n and μ_p are equal. The Hall coefficient is small if $\mu_n \sim \mu_p$.

Phonon drag has striking effects on both the thermoelectric and thermomagnetic coefficients. We consider here its influence on the Peltier coefficient in a particularly simple case, that of a semiconductor with a very low concentration n of charge carriers.

When an electric field E is applied to the material, it provides momentum to the charge carriers at the rate neE . If scattering by impurities and other defects can be neglected, all this momentum is passed on to the phonons. In the absence of phonon drag one would assume that this momentum becomes lost in random thermal vibrations, but here it must be supposed that the phonons can retain the momentum while they travel a distance l_d . Thus, if v is the velocity of sound waves, the momentum that is retained by the phonons at any given time is nel_dE/v .

Now the electric current density i is equal to $ne\mu E$, where μ is the carrier mobility. Furthermore, the heat flux density w due to the phonons is v^2 times their momentum. Thus the phonon-drag Peltier coefficient, equal to w/i , is given by

$$\pi_d = vl_d/\mu \quad (5.11)$$

The phonon-drag Peltier coefficient takes the same sign as the Peltier coefficient in the absence of phonon drag (which can be termed the electronic Peltier coefficient).

It might be thought that the free pathlength l_d can be calculated directly from the lattice thermal conductivity using Equation (3.24). However, the phonons that are responsible for the conduction of heat have a short wavelength, whereas the phonons that interact with the charge carriers in a semiconductor have a long wavelength. These long-wavelength phonons can have a particularly large mean free path, and it is this fact that makes the phonon-drag effects very great in some semiconductors. For example, a sample of p -type germanium has been found to have a phonon-drag Seebeck coefficient of more than 5 mV/deg at

25°K compared with a value of less than 1 mV/deg for the electronic Seebeck coefficient. Equation (5.11) shows that the phonon-drag effects should be largest for semiconductors in which the carrier mobility is relatively low and in which the mean free path of the long-wavelength phonons is very large; for example, a phonon-drag Seebeck effect has been observed up to a temperature of 700°K in conducting diamond.

Equation (5.11) suggests that the phonon-drag thermoelectric coefficients should be independent of the carrier concentration, and this is indeed true if the carrier concentration is small. However, when the carrier concentration is large, an appreciable proportion of the momentum that is passed on from the charge carriers to the phonons finds its way back to the carriers again. This reduces the phonon-drag coefficients, as does scattering of the charge carriers by impurities introduced in doping the semiconductor.

Symbols

A	cross-section area, atomic weight, lattice-dependent constant in Equation (4.1)
B	electron-dependent constant in Equation (4.1)
C	thermal capacity
C_v	specific heat per gram atom
E	electric field
F_D	Debye function
H	magnetic field
L	Lorenz number
L_0	high-temperature Lorenz number
N	Avogadro's number
P	Ettingshausen coefficient
Q	Nernst coefficient
R	Hall coefficient
S	Righi-Leduc coefficient
T	absolute temperature
U	internal energy per gram atom
U_0	internal energy per gram atom at 0°K
V	volume
W	potential energy
W_e	electronic thermal resistivity
W_0	electronic thermal resistivity due to impurity scattering
W_l	electronic thermal resistivity due to lattice scattering
a	lattice constant
b	constant in Equation (3.25)
c	specific heat, linear dimension of defect
c_p	specific heat at constant pressure
c_v	specific heat at constant volume
e	electronic charge
f	Fermi-Dirac distribution function
g	density-of-states distribution function
h	Planck's constant
i	electric current density

k	Boltzmann's constant, wavenumber of electrons
\mathbf{k}	wavevector of electrons
k_d	thermal diffusivity
l	length
l_d	mean free path of long-wavelength phonons
l_e	mean free path of electrons
l_t	mean free path of heat-conduction phonons
m	mass of free electron
m^*	effective mass
n	concentration of electrons, distribution function for normal modes, number of atoms per unit cell
p	pressure
q	phonon wavenumber
s	scattering parameter ($l_e \propto \varepsilon^s$)
t	time
u	internal energy per unit volume
v	velocity of sound
v_l	longitudinal sound velocity
v_t	transverse sound velocity
w	energy flux density
x	displacement
α	Seebeck coefficient, amplitude ratio
α_1, α_2	arbitrary force constants in Blackman's model
β	linear coefficient of expansion, phase difference
β_V	volume coefficient of expansion
γ	Grüneisen parameter
γ_e	electronic specific heat divided by absolute temperature
ε	energy of electrons
ε_g	energy gap
ζ	Fermi energy
ζ_0	Fermi energy at 0°K
θ_D	Debye temperature
κ	thermal conductivity
κ_e	electronic thermal conductivity

SYMBOLS

κ_L	lattice thermal conductivity
λ	wavelength
μ	carrier mobility
ν	frequency
ν_E	Einstein frequency
ν_m	maximum frequency of normal modes
π	Peltier coefficient
π_d	phonon-drag Peltier coefficient
ρ	density, electrical resistivity
ρ_0	electrical resistivity due to impurity scattering
ρ_l	electrical resistivity due to lattice scattering
σ	electrical conductivity
τ	Thomson coefficient
χ	compressibility
ω	angular frequency

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The thermal properties of
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THE THERMAL PROPERTIES OF SOLIDS

H. J. Goldsmid

The thermal properties of solids have, in the past, never attracted the same attention as the electrical properties, probably because they are much more difficult to measure accurately. Now, however, they are becoming of increasing significance in practical applications, particularly of the new electronic materials. For example, the thermal conductivity has an important role in determining the resistance of brittle materials to thermal shock, and is a vital parameter in controlling the efficiency of thermoelectric energy convertors. This book describes the various thermal effects arising from the atomic vibrations and the moving charge carriers. Particular emphasis is placed on the practical aspects of the subject, including the latest experimental techniques. Semiconductors are specially featured since they display several interesting phenomena that cannot be observed in other materials. There is a minimum of mathematics, though many useful formulae are given, their physical significance being explained. The book will prove invaluable to students of the pure and applied sciences, as well as to the practising engineer or technologist. A bibliography is provided for the many readers whose interest in the subject will be stimulated by this elementary treatment.

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